# Quality Assurance Project Plan for the Rappahannock, Corrotoman and York Rivers & Potomac River Virginia Embayments Shallow Water Monitoring (For the Period: January 1, 2009 through December 31, 2009)

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## 1. PROJECT DESCRIPTION

# 1.1 Project Definition and Background

The newest Bay agreement, <u>Chesapeake 2000: A Watershed Partnership</u>, states that "Improving water quality is the most critical element in the overall protection and restoration of the Chesapeake Bay and its tributaries" and further, it commits to "by 2010, correct the nutrient- and sediment-related problems in the Chesapeake Bay and its tidal tributaries sufficiently to remove the Bay and the tidal portions of its tributaries from the list of impaired waters under the Clean Water Act." In pursuit of this goal, the Bay partners agreed to "By 2003, the jurisdictions with tidal waters will use their best efforts to adopt new or revised water quality standards consistent with the defined water quality conditions."

The allocation of new monies in 2006 to increase Chesapeake Bay Monitoring and Assessment builds on the foundation of Federal-Interstate Bay Wide coordinated Chesapeake Bay Monitoring that is already in place. It greatly increases Virginia's ability to perform water quality assessment for preparation of the biennial 3035b/303d Integrated Report as well as the 2006 General Assembly House Bill 1150 (Chesapeake Bay and Virginia Waters Clean-up and Oversight Act. Virginia's regulatory definition of a "clean" Bay is attainment of water quality standards. Emphasis is on a newly developed sub-categories of aquatic life designated uses (i.e. Shallow Water, Open Water, Deep Water, Deep Channel, Migratory and Spawning) and associated numeric and narrative water quality criteria for dissolved oxygen, submerged aquatic vegetation (i.e. sea grass presence or water clarity, and phytoplankton (i.e. chlorophyll). The need to obtain water quality data to 1) evaluate the effectiveness of public fund expenditures to restore water quality in Virginia's Chesapeake Bay and 2) to assess attainment of the numeric water quality criteria is a critical element of the restoration and evaluation process.

EPA guidance on new water quality criteria for the Chesapeake Bay was published in April 2003. The development of these new water quality standards for turbidity (i.e. Kd), chlorophyll, and dissolved oxygen, have placed new requirements on accurate measurements of the temporal and spatial variability of water quality constituents. The development of the Surface Water Quality Mapping System (DATAFLOW) allows high speed, high resolution mapping of surface water quality from small vessels capable of sampling shoal and littoral areas. In addition, continuous measurements of water quality constituents are taken from fixed, shallow water monitoring stations using YSI underwater data sondes to assess temporal variability and the new weekly and instantaneous criteria. The combined application of these two technologies in this project allow the assessment of water quality criteria as well as an assessment of physical and biological processes controlling attainment or non-attainment. The work described in this plan is for 2009 and will add to the ongoing assessment work at VIMS to provide a comprehensive shallow water monitoring program of all the Virginia tributaries for application by the Virginia Commonwealth for assessing water

quality criteria and designated uses, and continued operation of the southern Chesapeake Bay atmospheric monitoring station. It remains consistent with and would provide further information to monitoring and assessment programs already in place in Virginia and Maryland. In addition, it provides an in depth, long-term understanding of water quality conditions in the Commonwealth's Chesapeake Bay tributaries and embayments that affect important living resources of those systems.

A total of seven (7) Chesapeake Bay Program (CBP) segments including the Rappahannock Mesohaline (RPPMH), Corrotoman Mesohaline (CRRMH), Rappahannock Oligohaline (RPPOH), Rappahannock Tidal Fresh (RPPTF), Potomac and Aquia Creeks (POTOH), seven embayments (Coan, Yeocomico, Lower Machodoc, Nomini, Mattox, Rosier and Upper Machodoc) in the Potomac Mesohaline (POTMH) and the York Polyhaline (YRKPH) will be sampled by this program in 2009 using continuous monitoring (CONMON), continuous buoy or fixed profilers, or monthly water quality mapping (DATAFLOW) sampling.

The table below illustrates the segments to be monitored, their designated uses and criteria parameters, and indicates if this project is expected to address these criteria.

	Open Wa	ater D.U.	Shallow Water D.U.	Spawning/Nursery D.U.
Segment	Chl-a	D.O. (1)	Kd	D.O. (1)
RPPMH	NA	YES	YES	NA
RPPOH	NA	YES	YES	YES
RPPTF	NA	YES	YES	YES
CRRMH	NA	YES	YES	NA
POTMH	NA	YES	YES	YES
РОТОН	NA	YES	YES	YES
YRKPH	NA	YES	YES	NA

NA: Criteria are not applicable to this designated use or this segment does not contain the designated use.

This project will also assist the CBP goal to "restore, enhance and protect the finfish, shellfish and other living resources, their habitats and ecological relationships to sustain all fisheries and provide for a balanced ecosystem" by collecting data useful for addressing the following issues:

- Temporally intensive water quality studies in vegetated and unvegetated shallows and adjacent channel areas in the Bay have demonstrated that differences in water quality between the two can be significant. Predictions of SAV transplant growth and survival using the closest available mid-channel, water quality monitoring data, have had poor success. Measurements of the spatial variability of water quality constituents, especially between channel and shoal regions and how this variability is related to SAV remains incomplete and will be enhanced through data collected by this study.
- Low levels of Submerged Aquatic Vegetation (SAV) in the Chesapeake Bay over the past 30 years have been related to sub-optimal water quality conditions. Conditions and

NO: Data from this project can not be used to assess these criteria.

YES: data from this project is expected to be used to assess these criteria.

<sup>1)</sup> Criteria are as instantaneous, 7-day mean, and 30-day mean values. Data from the DATAFLOW procedure can be assessed directly against instantaneous criteria and hopefully statistically extrapolated to assess against the 7-day and 30-day mean.

processes that influence water quality within the shallow littoral zones of the Chesapeake Bay and its tidal tributaries can be distinctly different from those in channel zones and can vary over short temporal and spatial scales. Recent EPA funded studies and their resultant peer-reviewed publications for high salinity regions of the Chesapeake Bay have demonstrated that water quality in vegetated shallows may be distinctly different from adjacent unvegetated shoal areas. Measurements of the spatial variability of water quality constituents in shallow waters longitudinally along Bay tidal rivers and how it is related to SAV remains incomplete and will be enhanced through data collected by this study.

- Suspended particles (both sediment and phytoplankton derived) are of particular concern as they can dominate light attenuation in the shallows and can be the principal factor limiting natural SAV recovery and SAV transplantation success in many formerly vegetated areas. Phytoplankton levels are principally related to nutrient and light availability while fine-grained suspended sediments originate from river inputs as well as from shoreline and bank erosion. Once they have entered the body of an estuary, however, sediments may be deposited and re-suspended many times through natural processes (tidal currents, wind, and waves). Physical processes in the shallows can also lead to increased levels of phytoplankton compared to channel regions, as the shallow mixing depths can reduce the effect of light limitation in these turbid areas. The synoptic collection of a wide suite of water quality and sediment parameters under this project will allow an assessment of physical and biological processes influencing water quality in shallow waters.
- The structure of the SAV community and its capacity to modify local conditions may provide a key to their continued survival or recovery in some areas where water quality is marginal for growth, or stresses are seasonal or pulsed in nature. Current modeling efforts include density dependent relationships between SAV density and particle loads and therefore water clarity. However, many estimates of statistically derived water quality conditions needed for SAV recovery have been obtained from water quality measurements in areas adjacent to existing beds. In some cases they may underestimate the levels of water quality improvements required for recovery into unvegetated areas, given sufficient capacity of SAV beds to improve conditions within the beds. Data collected under this project will allow for validation and enhancement of our current knowledge of SAV habitat requirements.
- An excessive concentration of phytoplankton is one of the main factors affecting poor water quality in the Chesapeake Bay and its tributaries. Excessive levels can indicate the presence of undesirable algae blooms that are of less value for fish and other predators to consume. Excessive phytoplankton play a direct role in reducing the amount of light available to SAV in shallow-water habitats and unconsumed algae sink to the bottom and decay, using up the oxygen required by many valuable organisms to survive.

• Dissolved oxygen (DO) is essential for animals living within the Bay. The amount of oxygen that can dissolve in water is strongly limited by the temperature of the water and, to a much smaller degree, by other substances dissolved in the water such as salt. The colder the water, the more oxygen it can hold. Most areas of the Bay with low DO are the result of a complex interaction of several natural and manmade factors. These factors include the amount of nutrients in the water, the way phytoplankton grow, die and decompose, the amount of fresh water flowing into the Bay, the Bay's bathymetry and the peculiar way in which water flows in estuaries such as the Chesapeake. The tolerance of animals to low oxygen levels can vary greatly. In some areas, such as surface waters or spawning and nursery areas, the tolerances of common organisms there for low dissolved oxygen are low. In other areas, such as the bottoms of deep channels, the organisms have adapted to the naturally low oxygen levels found there. Therefore the criteria and standards set for DO levels vary in both space and time for the Chesapeake Bay ecosystem.

The body of work, outlined in this Quality Assurance Project Plan, for the Rappahannock, Corrotoman Rivers and the Virginia Embayments and small tributaries of the Potomac River complements ongoing assessment work at VIMS and the State of Maryland. This program provides comprehensive monitoring of all of the Virginia tributaries, an integrated data management and analysis of shallow, open and deep water quality information for application by the Commonwealth to assessing water quality criteria. It remains consistent with and will provide further information to monitoring programs already in place in Virginia and Maryland. In addition, it will provide an in depth, long term understanding of water quality conditions in the Commonwealth's Chesapeake Bay tributaries and embayments that affect important living resources of those systems.

## 1.2. Objectives and Scope of Project

- 1) Collect data to be used in assessing water quality criteria for Dissolved Oxygen, Water Clarity, and Chlorophyll.
- 2) Collect data for diagnosing reasons for any non-attainment these water quality criteria.
- 3) Collect data to improve overall understanding and modeling of processes influencing these water quality criteria.
- 4) Collect data for refining our knowledge of non-regulatory SAV habitat conditions.
- 5) Provide calibration data for refined Bay Eutrophication and Watershed Model simulations of sediment transport, water clarity, phytoplankton, dissolved oxygen and SAV that will be completed over the next three years.

DATAFLOW sampling in 2009 will be conducted in six Chesapeake Bay Program segments including the Rappahannock Mesohaline (RPPMH), Corrotoman Mesohaline (CRRMH), Rappahannock Oligohaline (RPPOH), Rappahannock Tidal Fresh (RPPTF), and nine

embayments in the Potomac Mesohaline (POTMH) and Potomac Oligohaline (POTOH) segments (Coan, Yeocomico, Lower Machodoc, Nomini, Mattox, Rosier, Upper Machodoc, Potomac Creek and Aquia Creek). Collection of data from 0.25-0.5m below the surface will be performed monthly from April to October during critical SAV periods. The DATAFLOW system allows the continuous measurement of dissolved oxygen, chlorophyll, turbidity, salinity, specific conductivity, temperature, and pH while underway in a small boat. The data collected in any one day can then be interpolated to provide a complete surface "map" of water quality conditions throughout the segment that can then be compared against water quality criteria.

The specific goal of the fixed station continuous monitoring system is to assess water quality standards as well as quantify short-term variability and long-term changes in water quality constituents in specific shallow water areas. Five fixed continuous monitoring (CONMON) stations for 2009 will be located throughout the tidal Rappahannock River system with the following allocation: RPPMH (2 sites), RPPOH (1site), RPPTF (1 site), CRRMH (1 site) and one station each in the Potomac's Yeocomico, Nomini, Mattox Creek/Colonial Beach, Potomac Creek sites. In addition, the CONMON station located in the Mattox Creek/Colonial Beach area is real-time telemetered using the YSI EcoNet web-enabled monitoring and control system.

Concomitant data on chlorophyll and suspended sediment conditions are collected at single point sites during the dataflow mapping cruises and when the fixed stations sondes are exchanged. These data, for dataflow verification stations, will include: chlorophyll and pheophytin, total suspended solids (TSS), volatile suspended solids (VSS), dissolved oxygen using a YSI 600 XLM sonde, secchi depth, and vertical profiles of photosynthetically available radiation (PAR) and temperature, dissolved oxygen, salinity, specific conductivity, and pH. For the fixed stations this data will include: chlorophyll and pheophytin, total suspended solids (TSS), volatile suspended solids (VSS), dissolved oxygen by a YSI 6920 sonde, secchi depth, as well as a vertical profile for temperature, dissolved oxygen, salinity and pH and vertical profiles of photosynthetically available radiation (PAR). These data will be used to help assess the ecological conditions affecting the water quality criteria and provide enhanced monitoring data for refined Bay Eutrophication and Watershed model simulations of sediment transport water clarity, dissolved oxygen and SAV.

One fixed vertical profiling station in the YRKPH segment will be continued with profiles being made every hour from June through September 2009. The profiler is located on the US Coast Guard pier in the lower York River, latitude 37°13'35.94"; longitude 76°28'43.76". In addition, one buoy station with a vertical profiler will be initiated in the lower RPPMH segment, latitude 37°43'12.72"; longitude 76°34'0.78", with the assistance of CBNERRVA. Profiles will be made every hour at approximately 1 meter intervals in June through September 2009. Profiles will measure temperature, salinity, conductivity, dissolved oxygen, chlorophyll and turbidity using YSI 6600EDS V2 sondes.

All of this data, together with that collected by the VA DEQ mid-channel monitoring program will be used not only to assess criteria attainment, but also to evaluate the biological and physical processes controlling the criteria parameters. This data will also be helpful in further refinement of the habitat criteria needs of SAV, especially relative to the determination PLW (percent light through the water to SAV) and PLL (percent light to the SAV leaf). It will also assist in evaluating both DO and chlorophyll numeric and narrative standards and criteria relative to aquatic life designated uses. Finally, it will contribute to the evaluation of the effectiveness of public fund expenditures to restore water quality in Virginia's Chesapeake Bay and as a critical element of the continuing Bay restoration process.

# 1.3. Project Location Descriptions

# Rappahannock River System

This portion of the study will be conducted in the tidal Rappahannock River system, including its tributary, the Corrotoman River. Human population of the watershed for the year 2000 was estimated to be 240,754 individuals. Approximately 66% of the housing in the region is rural. Major population centers within the watershed include Culpeper, Falmouth, Fredericksburg, Orange, and Tappahannock Va. Land use is dominated by forest at 61% and agriculture at 39%. Nutrient and sediment loadings to the Rappahannock River are primarily from agricultural non-point sources. Sprague et al. (Factors Affecting Nutrient Trends in Major Rivers of the Chesapeake Bay Watershed. L.A. Sprague, M.J. Langland, S.E. Yochum, R.E. Edwards, J.D. Blomquist, S.D. Phillips, G.W. Shenk and S.D. Preston. U.S.G.S. WRIR #00-4218, 2000) described the Rappahannock River Basin as follows:

- The Rappahannock River Basin, at 2,800 sq. mi.,, is the fourth largest tributary basin in the Chesapeake Bay Watershed. The Rappahannock River originates near the eastern edge of the Blue Ridge Physiographic Provinces and extends eastward through the Piedmont and Coastal Plan Physiographic Provinces. The RIM station (01668000) is located at the Fall Line just upstream of Fredericksburg, VA. The monitoring station receives drainage from about 57% of the Rappahannock River Basin. Upstream from the monitoring station, the Rappahannock River Basin is of high relief, and the steep slope causes the river to respond rapidly to storm events.
- Land use upstream of the monitoring station is dominated by forest, at 61% and agriculture, at 36%. The Rappahannock River Basin contains the highest percentage of agricultural land above the Fall Line of the five tributary basins in Virginia. The agricultural areas above the monitoring station are generally located in the central part of the basin, in Faquier, Culpepper, Madison, and Orange Counties. Of the nine rivers in the RIM Program, the Rappahannock River contributes about 3% of the streamflow, 2% of the total nitrogen load, and 8% of the total phosphorus load delivered annually from the non-tidal part of the Chesapeake Bay Watershed.

# Potomac River System

This portion of the study will be conducted in the tidal Potomac River system. Human population of the watershed for the year 2000 was estimated to be 5,243,322 individuals. Land use is dominated by forest at 58% and agriculture at 32%, with approximately 5% of the land being developed. Sprague et al. (Factors Affecting Nutrient Trends in Major Rivers of the Chesapeake Bay Watershed. L.A. Sprague, M.J. Langland, S.E. Yochum, R.E. Edwards, J.D. Blomquist, S.D. Phillips, G.W. Shenk and S.D. Preston. U.S.G.S. WRIR #00-4218, 2000) described the Rappahannock River Basin as follows:

- The Potomac River Basin, at 15,570 sq. mi., is the second largest tributary basin in the Chesapeake Bay Watershed. The Potomac River drains a watershed composed of diverse physical settings and land use. The RIM station on the Potomac River (01646580) is located at the Fall Line near the northern Washington, D.C., boundary at Chain Bridge Road, about 1 mi upstream from where the Potomac River widens and becomes tidally influenced. Streamflow is measured 1 mi. upstream at Little Falls, MD. The RIM station receives drainage from 75% of the Potomac River Basin. Land use in the basin is about 61% forest, 35% agriculture, and 3% urban. Land use patterns are closely tied to the physical makeup if the basin and land use differs significantly in the basins of the major tributaries to the Potomac River.
- The westernmost tributaries, including the North and South Branch Potomac Rivers, drain the primarily forested Appalachian Plateau and the Valley and Ridge Provinces where farmland and small towns are located in the narrow river valleys. The Appalachian Plateau, the only coal-baring region, is drained by the uppermost tributaries of the North Branch Potomac River.
- The Great Valley extends across the center of the basin from near Waynesboro, VA., to Chambersburg, PA. The Shenandoah River and Opequon Creek drain the Great Valley from the south, and the Conococheague Creek and Antietam Creek drain the Great Valley from the north. Land use in the Great Valley is dominated by agriculture: however, the region has sizable urban areas and is experiencing significant urban and suburban development. Downstream from Harpers Ferry, W.VA., the Potomac River crosses the Blue Ridge Province, a pronounced ridge bounding the eastern edge of the Great Valley. This forested region contains many smaller streams that provide headwater drainage to Potomac River tributaries in the Great Valley and the Piedmont Provinces.
- The Piedmont Province is characterized by the gently rolling hills and has more varied land use than any other parts of the basin, with agricultural land dominating the northeastern portion and mixed forest, farmland, urban, and

suburban land throughout Virginia and Maryland. The density of urban and suburban development increases closer to Washington, D.C. The Monocacy River is the principal Potomac River tributary in the Piedmont, and many smaller streams drain directly to the Potomac River.

- The Coastal Plain Province and portions of the Piedmont drain to the tidal Potomac River downstream from the RIM station. Major tributaries include the Anacostia River in Maryland and the District of Columbia, and Occoquan River in Virginia. This region contains the most urbanized portion of the Potomac River Basin. Most major municipal wastewater treatment facilities in the metropolitan Washington, D.C., area discharge to the Potomac River downstream from the RIM station. Therefore, trends observed in water quality at the RIM station are not indicative of changes in wastewater discharge from the largest facilities in this basin.
- Of the nine Chesapeake Bay tributaries monitored, the Potomac River contributes about 20% of the streamflow, 28% of the total nitrogen load, and 33% of the total phosphorous load from the non-tidal portion of the Chesapeake Bay Watershed, making it the second largest streamflow and nutrient source to the Bay.

#### York River System

This portion of the study will be conducted in the tidal York River system. Population in the York River Basin for 2000 was projected to be 372,488. Major population centers within the watershed include Ashland, Gloucester Point, Hampton, and West Point, Va. Percentage of households within this basin is nearly equally divided between urban and rural areas, at 53% and 46%, respectively. Nutrient and sediment loadings to the York River are primarily from agricultural non-point sources. Sprague et al. (Factors Affecting Nutrient Trends in Major Rivers of the Chesapeake Bay Watershed. L.A. Sprague, M.J. Langland, S.E. Yochum, R.E. Edwards, J.D. Blomquist, S.D. Phillips, G.W. Shenk and S.D. Preston. U.S.G.S. WRIR #00-4218, 2000) described the York River Basin as follows:

- The York River Basin, at 2400 sq. mi., is the fifth largest tributary basin to Chesapeake Bay. The York River is formed by the confluence of the Pamunkey and Mattaponi Rivers near West Point, Va. Because these two sub-basins have distinct hydro-geological characteristics, they are monitored separately. The Pamunkey River begins in the eastern part of the Piedmont Physiographic Province and flows into the Coastal Plan Physiographic Province. The Pamunkey River RIM station (01673000) near Hanover, Va., receives drainage from about 45 percent of the York River Basin. The Pamunkey River sub-basin is of relatively low relief and contains Lake Anna approximately 60 miles upstream from the monitoring station. Lake Anna

serves to dampen and delay the hydroponic response of the Pamunkey River at the RIM station during storm events.

- The Mattaponi River sub-basin is located north of the Pamunkey River sub-basin, in the Piedmont and Coastal Plain Physiographic provinces. Because a relatively large percentage of the sub-basin is in the Coastal Plain, is of low relief, and contains expanses of wetlands, the Mattaponi River typically experiences lower stream flows and lower concentrations and yields of nutrients relative to the Pamunkey River and the other rivers draining to Chesapeake Bay. The Mattaponi River RIM station (01674500) near Beulahville, Va., receives drainage from about 25 percent of the York River Basin
- As with the other tributary basins in Virginia, land use in both sub-basins is dominated by forest. Forest makes up 68 percent of the land use upstream of the Pamunkey RIM station and 69 percent upstream of the Mattaponi River RIM station. Agriculture, the second largest land use at 24 percent and 19 percent respectively, is distributed sporadically throughout the sub-basins.

## 1.4. Project Dates

This is the third and final year of DATAFLOW and CONON data collection in the Rappahannock River System and the Virginia Embayments of the Potomac. The time period for this study is from January 1, 2009 through December 31, 2009. This is the first year of the Rappahannock vertical profiling buoy data collection. Continuation of the York River and Rappahannock River vertical profilers will be subject to future funding. Semi-Annual progress reports will be delivered in accordance with the dates stipulated under deliverables in the contract.

## 1.5. Data Quality Objectives

The main objective of this program is to collect data of sufficient quantity and quality to assess Bay water quality criteria and standards for chlorophyll, water clarity, and dissolved oxygen. This data must be representative and comparable across all the monitored tributaries. Existing monitoring programs collect data monthly at a few specific mid-channel station locations at bi-weekly to monthly intervals of time. For parameters such as turbidity (water clarity), dissolved oxygen and chlorophyll, conditions in the shallow water areas, which are important for natural resources such as submerged aquatic vegetation, can be quite different than in the mid-channel regions. There is inherent error in using mid-channel data to represent shallow water areas, and also using a small number of single points to represent an entire system. This monitoring program not only generates data in these important shallow areas, it also covers the channel areas to a much greater extent spatially (via

DATAFLOW). This greater spatial and temporal density of data which can be used to assess surface water quality criteria and standards is an important component of this monitoring program. Another strength of the program is the comparability of data with that collected by our Maryland partners in the northern Chesapeake Bay, as well as other Chesapeake Bay Monitoring Programs. Through the use of the same Chesapeake Bay Program approved protocols, instrumentation, quality control checks, and communication, a integrated net of data is generated for the Bay.

# 2. PROJECT ORGANIZATION AND RESPONSIBILITIES

# 2.1. Project Organization

The collection and preparation of samples, plus data entry and management will be completed at the Virginia Institute of Marine Science under the direction of Dr. Kenneth A. Moore (PI) and Dr. William Reay (Co-PI). The VA Department of Environmental Quality project officer will be responsible for general oversight and assuring that project objectives meet Federal-Interstate Chesapeake Bay program goals. Coordination of data collection protocols with similar investigations occurring in other Chesapeake Bay waters is performed through the Tidal Monitoring and Assessment Workgroup of the Chesapeake Bay Program Monitoring and Assessment Subcommittee. All water quality analyses are performed by VIMS Analytical Services Center (ASC).

# 2.2. Principal Investigator

The principal investigator (PI), Dr. Kenneth Moore (moore@vims.edu, 804-684-7384), will supervise all activities associated with this project. This includes fieldwork, data management and report writing. He will be responsible for all stages of the analysis of samples, resolving problems that may arise, and assure the satisfactory completion of the study. He is responsible for data review and oversight and submission of data. The PI will review the results of the analyses and approve the quality assurance/quality control protocols to insure the validity of the results. The PI will administer the financial and technical requirements of the project and be responsible for preparing the data and progress report and the final report to be submitted at the end of the project. He will also meet, at regular time intervals, with the other members of staff to discuss and review their responsibilities in relation to the project. The PI will respond to questions by the contracting agencies regarding the completion of different stages of the project and the reports that have to be submitted as part of the deliverables outlined in the project contract. Dr. Kenneth Moore holds a B.S. degree in Biology from The Pennsylvania State University, a M.S. degree in Marine Science from the University of Virginia and a Ph.D. degree in Marine, Environmental and Estuarine Science from the University of Maryland.

The Co-PI, Dr. William Reay (<u>wreay@vims.edu</u>, 804-684-7119), will co-supervise the activities associated with the continuous, fixed station monitoring including protocol

development, station setup, fieldwork, and data management. He will work with Dr. Moore on report writing, QA/QC and other aspects of the overall monitoring program. Dr. Reay is the Director of the Chesapeake Bay National Estuarine Research Reserve in Virginia (CBNERRVA). Prior to that position he was Director of Research at CBNERRVA and initiated the system wide nutrient and fixed station monitoring program in Virginia. His research interests include physical transport mechanisms of nutrients within riparian and littoral zones, biotic and abiotic processes that influence nutrient fluxes within these environments, and the impact of these loadings on surface water resources. Dr. Reay holds a B.S. degree in Biology from George Mason University, a M.A. degree in Marine Science from the College of William and Mary and a Ph.D. in Biology from Virginia Polytechnic Institute and State University.

# 2.3. Personnel Qualification Summary

Mrs. Betty Neikirk (betty@vims.edu, 804-684-7400) is a Marine Scientist Supervisor at VIMS and holds a B.S in Biology from Randolph-Macon College and a M.S. in Marine Science from the College of William and Mary. Mrs. Neikirk is the Quality Assurance Officer for the Shallow Water Monitoring Program. She has been involved with water quality research and monitoring at VIMS for 25 years and oversees the DATAFLOW and CONMON (Continuous Monitoring) field programs, has responsibility for data analysis, coordinates and schedules all field operations, as well as participates in the field operations. She reports to the principal investigator.

Mrs. Joy D. Austin (justjoy@vims.edu, 804-684-7307) is a Laboratory & Research Specialist II/Laboratory Supervisor at the Virginia Institute of Marine Science. She is currently in charge of the day-to-day activities of the water quality and fixed station monitoring at CBNERRVA and is familiar with all aspects of CBNERRVA monitoring. She will be responsible for overseeing the continuous, fixed station monitoring activities including activities such as sonde calibration, QA/QC of data and data management, sampling coordination, purchases of equipment and supplies. She will coordinate fixed station activities with Mrs. Betty Neikirk

Mr. David Wilcox (dwilcox@vims.edu, 804-6847088) is a GIS specialist at VIMS and holds a B.S. in Mathematics from Virginia Tech University and a M.S in Geography from Ohio State University. He will review GIS data analysis of the high frequency spatial data and will assist in the development of the two dimensional maps of the surface water quality conditions using GIS.

Mr. Jim Goins (goins@vims.edu, 804-684-7559) is a Laboratory & Research Specialist II /Field Manager at VIMS. He will help conduct the field sampling activities associated with this project including; Dataflow mapping, water quality verification sampling and fixed station sampling and participates in other monitoring programs as needed. He has extensive

small vessel handling experience, and holds US Coast Guard Basic Seamanship and Safety and VIMS small vessel certification

Mr. Steve Snyder (snyder@vims.edu, 804-684-7442) is a Laboratory and Research Specialist II at VIMS who holds an Associates Degree in Applied Science from Thomas Nelson Community College. He assists in the field and laboratory work related to this project including the dataflow mapping, water quality verification sampling and the calibration of the instruments. He also has extensive small vessel handling experience and holds US Coast Guard Basic Seamanship and Safety and VIMS small vessel certification.

Mr. Voight Hogge (voight@vims.edu, 804-684-7087) is a Laboratory and Research Specialist I at VIMS and is a Master Captain with a 50 ton license. He has extensive boating experience as well as knowledge of local water ways. He will be working as a boat captain assisting with the field effort associated with the DATAFLOW and Continuous Monitoring Programs. Mr. Hogge will also be doing routine boat maintenance. In addition to his captain's license, Mr. Hogge holds a US Coast Guard Basic Seasmanship and Safety and VIMS small vessel certification.

Mr. Jeremiah Walawender (jeremiah@vims.edu, 804-684-7087) is a Laboratory and Research Specialist I at VIMS who holds a BS degree in Biology from Chowan College. Mr. Walawender plays a key role in the field effort associated with the DATAFLOW and Continuous Monitoring Programs. He also has small vessel handling experience and holds US Coast Guard Basic Seamanship and Safety and VIMS small vessel certification.

Ms. Alynda Miller (<u>alynda@vims.edu</u>, 804-684-7576) is a Laboratory and Research Specialist II at VIMS. She has a B.S. in Biology from the Millersville University of Pennsylvania. She will aid in the fixed monitoring program including activities such as sonde calibration, QA/QC of data and data management, sampling coordination, purchases of equipment and supplies.

Ms. Amber Knowles (amber@vims.edu, 804-684-7576) is Laboratory and Research Specialist I at VIMS. She has a B.S. in Biology from Mary Washington College. She will aid in the fixed monitoring program including activities such as sonde calibration, sample filtration, and maintaining equipment and preparation of field supplies.

Mr. David Parrish (parrishd@vims.edu, 804-684-7835) is a GIS Analyst at the Virginia Institute of Marine Science and holds a B.S. in Integrated Science and Technology from James Madison University and an M.S. in Natural Resource Management from Central Washington University. He conducts the spatial and statistical analysis to evaluate water quality criteria attainment in Virginia waters and generate spatial imagery for the VECOS website. Mr. Parrish provides GIS support to the program and manages the VECOS (www.vecos.org) database and website.

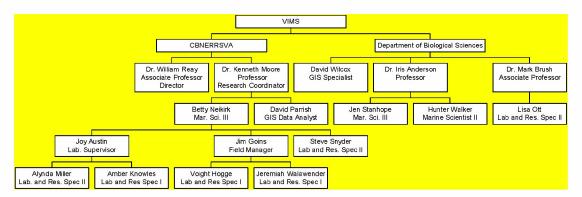
Mrs. Carol Pollard (pollard@vims.edu, 804-684-7213) is a Laboratory Director/Scientist II (Supervisor). She has a B.S. in Environmental Science from Florida Institute of Technology and a M.S. in Marine Science from the College of William and Mary. Mrs. Pollard is the Director of the Analytical Services Center at the Virginia Institute of Marine Science. Her responsibilities include lab goals, budget, coordinating personal and maintaining safety and quality control. Mrs. Pollard also coordinates with the Virginia Department of Environmental Quality and the U.S. Environmental Protection Agency in blind audits, cross laboratory calibration samples and the Chesapeake Bay Program's Coordinated Split Sample Program (CSSP).

Mr. Todd Nelson (nelson@vims.edu, 804-684-7283) is an Electronics Technician III at VIMS and holds an Associates degree in Applied Sciences from the Gillford Technical Community College and a BA in psychology from University of North Carolina at Greensboro. He provides technical expertise in the development and maintenance of the DATAFLOW equipment including software programming, implementation of equipment upgrades, and trouble shooting.

Dr. Mark Brush is an Associate Professor of Marine Science (<a href="mailto:brush@vims.edu">brush@vims.edu</a>) and Dr. Iris Anderson a Professor (iris@vims.edu) will oversee operation of the York River Fixed Buoy. Jen Stanhope, a Marine Scientist III (<a href="mailto:jwu@vims.edu">jwu@vims.edu</a>) has the responsibility for overseeing sampling and data analyses and quality assurance of the York River Fixed Buoy system. Hunter Walker (<a href="mailto:hunter@vims.edu">hunter@vims.edu</a>) and Lisa Ott (<a href="mailto:ott@vims.edu">ott@vims.edu</a>) are responsible for Buoy sonde calibration and field sampling of the York River Buoy.

All of the above personnel are located at VIMS, P.O. Box 1346, Gloucester Point, VA 23062.

# 2.4. Organizational Chart



## 2.5. Special Training and Certification

Vessel certification is required for use of all small boats at VIMS. This includes successful completion of US Coast Guard approved small vessel navigation and safety course and a yearly renewable, vessel-specific certification by the VIMS Vessels Center. A current list of approved small vessel operators can be found at the web site: <a href="http://www.vims.edu/admin/vessels">http://www.vims.edu/admin/vessels</a>.

#### 3. SAMPLING PROCEDURES

# 3.1. Continuous Surface Water Quality Mapping in the Rappahannock River System & the Virginia Embayments of the Potomac River

## 3.1.1. DATAFLOW Mapping system

DATAFLOW is a compact, self-contained surface water quality mapping system, suitable for use in a small boat operating at speeds of about 25 KT. The system collects water through a pipe ("ram") deployed on the transom of the vessel, pumps it through an array of water quality sensors, and then discharges the water overboard. The entire system from intake ram tube to the return hose are shielded from light to negate any effect high intensity surface light might have on phytoplankton in the flow-through water that is being sampled. A blackened sample chamber is also used to minimize any effect of light on measurements by the fluorescence probe.

## 3.1.2. Area of Operations, Cruise Tracking, and Sample Frequency

The area of operations will include the Rappahannock River System as well as the Virginia Embayments of the Potomac River. This area includes five of the EPA Chesapeake Bay Program Office's designated Chesapeake Bay segments (see

www.chesapeakebay.net/pubs/segmentscheme.pdf for description of CBP segments). They include the Rappahannock River Mesohaline (RPPMH), the Rappahannock River Oligohaline (RPPOH), the Rappahannock River Tidal Fresh (RPPTF), and the Corrotoman River Mesohaline (CRRMH). The Virginia Embayments of the Potomac River include the Coan River (POTMH\_COA), the Yeocomico River (POTMH\_YEO), the Lower Machodoc River (POTMH\_LMA), the Nomini River (POTMH\_NOM), Mattox Creek/Monroe Bay (POTMH\_MAT), Rosier Creek (POTMH\_ROS), Upper Machodoc Creek (POTMH\_UMA), Potomac Creek (POTOH POM), and Aquia Creek (POTOH AQU).

Cruises are scheduled to take place monthly from April 2009 to October 2009. Each segment is monitored on a separate, single day (i.e. one segment per day). All cruise dates are dependent on weather conditions optimum for the safety of the field crew, tide stage for some segments, and ability to attain quality data. Cruises which have to be cancelled due to weather conditions will be rescheduled at a later date. Cruises will take place during the mid day, over an approximate four to five hour interval beginning at approximately 0900 to 1000.

Operations follow different cruise tracks depending on the morphology of the segment being monitored and the amount of navigable shallow water. In the lower segments of the rivers, where the width of the river is normally wide, a series of tracks running parallel to the shoreline along fixed depth contours is followed. The track follows the shoreline down river along the ≤2 meter depth contour, then up river along a mid depth contour (approximately 5 meters), it then goes down river along the channel (>10 meters depth), then finish an up river leg along the other shoreline in the shallows. Further up the rivers, the width narrows and there is less safe shallow water. In these areas two parallel passes are made in the river, as close to the shallows as possible. In the upper tidal fresh regions where the bathymetry contains very little navigable shallow water and the waters are relatively narrow multiple tracks are not necessary and the area may be monitored with one pass. Due to the likely presence of many navigational hazards and limitations due to sea conditions, the actual cruise track will be adjusted on the day of operations as necessary.

The DATAFLOW mapping system collects a sample once every 3-4 seconds. The resulting distance between samples is therefore a function of vessel speed. Vessel speeds vary throughout the cruise depending on depth of water, navigational hazards, weather conditions and the slowing of the vessel approaching or leaving verification stations. Average speed underway is approximately 20 knots, which results in an observation collected every 30 meters. As speeds decrease this means samples will occur closer together, but for the most part when underway between the speeds of 10-20 knots samples will occur every 15-30 meters. Five stations for verification samples will also be sampled at intervals along the cruise track, within each CBP bay segment.

## 3.1.3. Water Quality Instrumentation

The DATAFLOW system has a YSI 6600 sonde equipped with a flow-through chamber. The sensors include a Clark-type 6562 DO probe, a 6561 pH probe, a 6560 conductivity/temperature probe, a 6136 turbidity probe, and a 6025 chlorophyll probe. The sonde transmits data collected from the sensors directly to a Panasonic Toughbook, ruggedized laptop computer using a data acquisition system created with LabView software (National Instruments, Inc.). Custom software written in the Labview environment provides for data acquisition, display, control, and storage. Real-time graphs and indicators provide feedback to the operator in the field, ensuring quality data is being collected. All calibrations and maintenance on the YSI 6600 sondes are completed in accordance with the YSI, Inc. operating manual methods (YSI 6-series Environmental Monitoring Systems Manual; YSI, Inc. Yellow Springs, OH).

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PARAMETER	UNITS	PRECISION	ACCURACY	MDL
DO	% Saturation	0.1%	± 2%	0 %
DO	mg/L	0.01mg/L	±0.2mg/L	0 mg/L
Salinity	ppt	0.01ppt	0.1ppt	0 ppt
Temperature	°C	0.01°C	±0.15°C	-5°C
рН	unit	0.01units	±0.2units	0 units
Turbidity	NTU	0.1NTU	2 NTU	0 NTU
Chlorophyll	μg/L Chl	0.1μg/L Chl	-	0 μg/L Chl

#### 3.1.4. Positioning, Depth Information and Data Acquisition

The DATAFLOW system is equipped with a Garmin GPSMAP 540s with sounder. This unit serves several functions including chart plotting, position information, and depth. The unit is WAAS (Wide Area Augmentation System) enabled providing a position accuracy of better than three meters 95 percent of the time. The NEMA 0183 data sentence containing all pertinent position and depth information is output to the SBC data acquisition system.

The DATAFLOW system utilizes a SBC data acquisition system for data collection and storage. The system is based on a Panasonic Toughbook, ruggedized laptop computer. Custom software written in a Labview environment provides for data acquisition, display, control, and storage. All data is collected simultaneously in one file, removing the chore (and possible errors) of merging separate files into one.

## 3.1.5. Cruise Scheduling

Monthly cruises have been scheduled for the 2009 season. The Rappahannock & Corrotoman Rivers will be covered on five consecutive days of cruises. The Potomac

Embayments will be covered in two consecutive days. As stated previously cruise dates are subject to change due to inclement weather conditions or mechanical problems with the research vessel. A schedule for activities for each day of the individual cruises is submitted to the PI and other members of staff. Cruises that are cancelled due to weather or mechanical problems with the research vessel are rescheduled.

### 3.1.6. Sampling Procedures

#### 3.1.6.1. Real-Time Field Verification

The DATAFLOW system provides field personnel with a real time display of parameters as the data is being collected. The field crew, who are knowledgeable and experienced in estuarine water quality monitoring, accesses this data in real time. The crew has a working knowledge of the normal water quality conditions and how weather patterns, diurnal patterns, seasons, and events such as algal blooms might affect data. When unusual results are observed, action is taken to investigate the cause of the unusual data and either note the cause or take action to correct any equipment issues that may be contributing factors. There are various factors which can lead to erroneous data including; fouling of the ramjet intake, wiper malfunction on the optical probes, probe failure, etc. When these conditions are observed the affected part of the data record is noted in the field notes. During the data review the Quality Assurance Officer takes these notes into account and flags the data accordingly. At verification stations, dissolved oxygen, pH, salinity and temperature are verified using a YSI 600 XLM. If there is a greater then 0.5mg/l difference in dissolved oxygen, 0.2 SU difference in pH, or greater than 1 degree Celsius difference between instruments this is investigated and corrective action is taken. This usually involves switching the YSI 6600 for the spare that is carried on board the research vessel. Close attention is also given to YSI 6600 chlorophyll and turbidity and if readings are questionable the YSI 6600 is switched out with the spare on board.

# 3.1.6.2. Verification Sample Collection

A total of five verification stations will be sampled along the cruise track in each CBP Bay segment. Stations are selected to maximize the range of values that are seen along a track (e.g. when moving up a tributary with a salinity gradient, samples are taken to get a high, medium, and low salinity value). Within each segment, the fixed monitoring stations from this program as well as the stations from the VA Department of Environmental Quality's tributary monitoring program will be utilized as verification stations. Extra sampling supplies will be available to sample more stations under special conditions such as in areas of large blooms. At each station the boat is stopped and water samples are collected from the effluent tubing of the DATAFLOW System (sampling water depth of approximately 0.25 - 0.50 m) for total suspended solids (TSS), volatile suspended (VSS), chlorophyll, and pheophytin. At these stations secchi depth, a vertical profile of photosynthetically available radiation (PAR), as well as a vertical profile for temperature, dissolved oxygen, salinity and

pH are also done (See Appendix D for further details). Samples for TSS, VSS, chlorophyll and pheophytin are collected in darkened bottles, which are rinsed three times with ambient water before filling. Samples for chlorophyll and pheophytin are filtered on board the vessel. (See Appendix D for further details). These are then packed on ice in a darkened cooler, and returned to the laboratory where they are stored at -20°C. Samples for TSS and VSS are packed on ice, in a darkened cooler, and returned to the laboratory where they are filtered immediately upon return and frozen (Appendix D). Samples are then delivered to the VIMS Analytical Service Center for further processing.

# 3.1.6.3. Vertical Profile of Dissolved Oxygen, Water Temperature, and Salinity

A vertical profile of the water column is accomplished using a YSI 600 XLM which includes a Clark-type YSI 6562 DO probe, a YSI 6560 conductivity/temperature probe, and a 6561 pH probe. This profile includes water temperature, specific conductivity, salinity, dissolved oxygen and pH. At the shallow water verification stations (water depth less than 2 meters), this is accomplished by placing the sensor at a 0.1 meter depth, letting it equilibrate and recording the measurements. The same procedure is then followed at successive 0.25 m intervals thereafter until the final reading is taken approximately 5 cm above the bottom. At deep-water verification stations the YSI is lowered until the bottom is reached. This depth will be rounded to the nearest meter and then the sonde will be pulled to 1 meter above the bottom and allowed to equilibrate. Measurements will be recorded and then the sonde will be raised through the water column stopping at each 1 meter interval to allow equilibration and recording of readings until a depth of 1 meter below the surface has been reached. All calibrations and maintenance on the YSI 600 XLM sonde is completed in accordance with the YSI, Inc. operating manual methods (YSI 6-series Environmental Monitoring Systems Manual; YSI, Inc. Yellow Springs, OH).

# 3.1.6.4. Field Duplicates

At one verification station, during each individual sampling event, a duplicate sample for all sample types and measurements will be taken. The duplicate information will be used to assess the precision of the sample results and measurements. Field duplicates are taken in quick succession with the initial sample from the outflow of the DATAFLOW system, in separate sample bottles. The precision of field duplicate pairs will be assessed by a combination of relative percent difference (RPD) based on the previous year's average RPD, and absolute difference. If a duplicate's RPD falls outside of two (2) standard deviations of the average it will be considered a warning, outside of three (3) standard deviations is considered failure. Under both circumstances, investigation into the possible source of the issue will ensue.

#### **3.1.6.5. Field Blanks**

Artificial sample contamination in the field represents an issue of concern for chlorophyll sampling equipment and bottles. To address these concerns the sample bottles and equipment are prepared and cleaned according to the procedures indicated in Section 4.1.2. Field blanks are collected by processing DI water through the filtration apparatus (including filters) while on location at one verification station per individual field event. Field results will be used to determine if contamination has occurred in the sampling process. Decisions to invalidate associated project data on the basis of artificial sample contamination will be made based on a comparison of the field blank with the lowest analytical standard in the calibration curve and the detection limit for each parameter. If the concentration of a field blank exceeds the lowest analytical standard in the calibration curve field and/or laboratory contamination is suspected, corrective action will be initiated. This will include investigation of possible contamination sources (both in the field and in the laboratory) as well as potential procedural modifications to alleviate the problem.

## 3.1.6.6. Field Documentation and Records

All field data are recorded on specially prepared field data sheets. The raw data sheets are reviewed for possible missing data values due to sample collection problems prior to data entry. These sheets are initialed and filed by the Quality Assurance Officer/Data Manager.

# 3.2. Fixed Station Water Quality Monitoring in the Rappahannock River System & the Virginia Embayments of the Potomac River

# 3.2.1. Fixed Monitoring Stations Description

Fixed monitoring stations are located throughout the Rappahannock and Corrotoman Rivers as well as in the Virginia Embayments of the Potomac. These fixed stations are used to continuously monitor water quality parameters including depth, water temperature, salinity, pH, chlorophyll, turbidity, and dissolved oxygen using YSI 6600EDS V2 data sondes. These stations will provide long term measurements that can be supplemented with shorter term monitoring, such as the DATAFLOW cruises, and other process-oriented studies.

The fixed stations are designed to be deployed off existing piers or other structures within a locked 4 inch PVC housing. This housing is perforated to allow flow of water freely to the instrument while at the same time protecting the instrument from large pieces of floating debris. The stations are placed at a depth of 1.0 to 1.5 meters MLW. Within the PVC housing, an YSI 6600EDS V2 data logging sonde is secured 0.5 meters above the bottom. The PVC pipe structure is cleaned with a chimney sweep type tool at each switch out to reduce fouling and the collection of sediment on the inside of the pipe.

# 3.2.2. Locations of Fixed Monitoring Stations and Sample Frequency

There are a total of nine continuous monitoring stations; two in the Rappahannock Oligohaline, one in each of the other segments to be monitored and one each in the four Virginia Potomac River Embayments (Appendix A). The continuous monitoring station locations were chosen to provide coverage in the each of the Bay monitoring segments in the Rappahannock and Corrotoman Rivers as well as in four of the Virginia Embayments of the Potomac River. While the main stem Potomac River was monitored in 2006, 2007 and 2008 by Maryland, the large shallow embayments of the Potomac in Virginia have gone largely unmonitored. These embayments are important areas for SAV growth. The following table gives the approximate locations of the stations.

Locations of Fixed Stations within the Rappahannock, Corrotoman and Potomac Rivers 2009

111111111111111111111111111111111111111				
Fixed Station	Location	CBP Segment	Latitude	Longitude
#1	Christchurch School	RPPMH	37.62083	-76.54645
#2	Bowlers Wharf	RPPMH	37.82195	-76.75027
#3	Kendale Farm	RPPOH	38.08072	-76.96395
#4	Hick's Landing	RPPTF	38.18543	-77.24062
#5	Corrotoman River	CRRMH	37.69735	-76.46817
#6	Potomac Creek	РОТОН	38.34360	-77.30485
#7	Colonial Beach (Mattox	POTMH	38.23197	-76.96372
	Creek/Monroe Bay)			
#8	Yeocomico River	POTMH	38.02878	-76.55184
#9	Coan River	POTMH	38.13160	-76.71759

Individual YSI 6600EDS V2 sondes will be deployed for a maximum of 14 days on permanently established stations, where they will log data at 15-minute intervals. Deployment length is adjusted for areas and periods of high fouling. At the end of the deployment period each YSI sonde is returned to the lab for downloading of data, post calibration, cleaning, membrane replacement, and re-calibration. A second YSI 6600EDS V2 is deployed following retrieval of the original sonde in order to maintain a continuous record of data. The two sondes are placed adjacent to one another for 20 minutes to allow for post comparison of the individual units and to allow for no loss of monitoring data.

## 3.2.3. Water Quality Instrumentation

The fixed stations utilize the YSI 6600EDS V2 equipped with the Clean Sweep Extended Deployment System (EDS) and with sensors including a ROX 6150 Optical DO probe, a YSI 6560 conductivity/temperature probe, a 6561 pH probe, a 6136 turbidity probe, and a 6025

chlorophyll probe. The EDS is comprised of a brush that at set intervals sweeps across the sensors to dislodge any fouling organisms or material that has settled on the sensors. This feature ensures better quality data over longer deployment periods in areas with high fouling rates. The new YSI ROX DO probe utilizes the luminescence-lifetime technique to provide DO measurements which are less likely to be affected by fouling or low DO environments.

Quality of YSI Data (YSI 6600EDS V2)

PARAMETER	UNITS	PRECISION	ACCURACY	MDL
ODO	% Saturation	0.1%	±1%	0 %
ODO	mg/L	0.01mg/L	±0.1mg/L	0 mg/L
Salinity	ppt	0.01ppt	0.1ppt	0 ppt
Temperature	°C	0.01°C	±0.15°C	-5°C
рН	unit	0.01units	$\pm 0.2$ units	0 units
Turbidity	NTU	0.1NTU	2 NTU	0 NTU
Chlorophyll	μg/L Chl	0.1μg/L Chl	•	0 μg/L Chl

# 3.2.4. Schedule of Maintenance and Sonde Exchange

Sondes are deployed for a maximum of 14 days. Upon return to the laboratory the sondes are post calibrated, cleaned, and routine maintenance is performed as needed. The sondes are then stored until they are calibrated just prior to their next deployment. All calibrations and maintenance are completed in accordance with the YSI, Inc. operating manual methods (YSI 6-series Environmental Monitoring Systems Manual; YSI, Inc. Yellow Springs, OH). See Appendix C for more detailed information.

## 3.2.5. Sampling Procedures

#### 3.2.5.1. Verification Samples

Field verification of pH, salinity, dissolved oxygen and temperature are taken during the deployment/retrieval procedure with a YSI 6920 sonde. Water samples for total suspended solids (TSS), volatile suspended (VSS), chlorophyll-a, and pheophytin are taken when the YSIs are switched out at the depth of the instrumentation. Chlorophyll and pheophytin water samples are immediately filtered and the filter stored in sterile Whirlpak bags (See Appendix D for further details). These are then packed on ice and returned to the laboratory where they are stored at -20°C. Samples for TSS and VSS are packed on ice and returned to the laboratory where they are filtered immediately upon return and frozen (Appendix D). Samples are then delivered to the VIMS Analytical Service Center for further processing. At these stations secchi depth, a vertical profile of photosynthetically available radiation (PAR), as well as a vertical profile for temperature, dissolved oxygen, salinity and pH are also done (See Appendix D for further details).

The data being gathered by the original YSI 6600EDS V2 is also verified by placing the new YSI 6600EDS V2 into the water beside it for a 20 minute time period at the end of its deployment. The two data sets can then be compared to determine that the YSIs are functioning correctly.

# 3.2.5.2. Vertical Profile of Dissolved Oxygen, Water Temperature, and Salinity

A vertical profile of the water column is accomplished using a YSI 6920 which includes a ROX 6150 Optical DO probe, a YSI 6560 conductivity/temperature probe, and a 6561 pH probe. This profile includes water temperature, specific conductivity, salinity, and dissolved oxygen and pH. This is accomplished by placing the sensor at a 0.1 meter depth, letting it equilibrate and recording the measurements. The same procedure is then followed at successive 0.25 m intervals thereafter until the final reading is taken approximately 5 cm above the bottom. All calibrations and maintenance on the YSI 6920 sonde is completed in accordance with the YSI, Inc. operating manual methods (YSI 6-series Environmental Monitoring Systems Manual; YSI, Inc. Yellow Springs, OH).

3.2.5.3. Summary Table of Monitoring Parameters

PARAMETER	COLLECTION PROCEDURE	PRES ER- VATI ON	PERFORMS ANALYSIS	DETECTION LIMITS	CBP (CIMS) METHOD (unless noted otherwise)
Temperature	YSI 6600V2/6920		Field		F01
рH	YSI 6600 V2/6920		Field		F01
Dissolved Oxygen	YSI 6600 V2/6920		Field		F01
Specific Conductivity	YSI 6600 V2/6920		Field		F01
Salinity	YSI 6600 V2/6920		Field		F01
Fluorescence	YSI6600 V2		Field		NA
Chlorophyll	YSI6600 V2		Field		F01
Secchi Depth	Secchi Disk		Field		F01
PAR Light Attenuation	Li-Cor		Field		F01
Total Suspended Solids	Whole water	ICE	ASC	1.4 mg/l	L01
Fixed Suspended Solids	Whole water	ICE	ASC	2.5 mg/l	L01
Volatile Suspended Solids	Whole water	ICE	ASC	2.5 mg/l	L01
Chlorophyll a	GF/F Filter 47 mm diameter 0.7 um pore size	ICE	ASC	0.50 ug/L	L03
Phaeophytin a	GF/F Filter 47 mm diameter 0.7 um pore size	ICE	ASC	0.50 ug/L	L03

#### 3.2.5.4. Field Documents and Records

All field data are recorded on specially prepared field data sheets. The initials of the person recording the data are recorded on each data sheet. The raw data sheets are reviewed for possible missing data values due to sample collection problems prior to data entry. These sheets are filed with the Laboratory Supervisor.

# 3.3. Pontoon- based and Pier- based Vertical Profile Water Quality Monitoring in the Rappahannock and York Rivers

Complete field sampling procedures are documented in "Quality Assurance Project Plan for the York River Open and Deep Water Monitoring (For the Period: April 1, 2007 through October 31, 2008). Protocols will also apply to the Rappahannock vertical profiler.

## 4. DATA MANAGEMENT PROCEDURES

## 4.1. QA/QC Field Checks

The objectives of QA/QC standards are to provide accurate measurement of water quality and SAV parameters in the Rappahannock, York, and Potomac River Systems. Over the 15 years that the VIMS SAV water quality research group has been making similar measurements, consistent protocols have been developed in the field. Together with laboratory procedures already in place and used by the Analytical Services Center (ASC) and data management procedures, the data obtained can be analyzed and interpreted so that the final report submitted will meet the objectives stated for this study. Information derived from the report will be useful to managers making decisions concerning these areas, as well as comparable to water quality data being generated by the Maryland partners in this monitoring project.

# 4.1.1. Preparation of Field Gear

During the few days prior to initiating a DATAFLOW or sonde deployment/retrieval cruise all the necessary equipment involved in the collection of water samples and of physical water quality data are inventoried according to "checklists." All equipment is checked to insure that it is fully operational and has been properly cleaned. The equipment is packed into containers that provide for easy transport and loaded aboard the research vessel. The "checklist" is then re-examined to verify the presence of all necessary gear. Standards and reagents used in the calibration of instrumentation are made according to a schedule of shelf life or if the supply is exhausted. All chemicals are handled, prepared, and stored in accordance with standard laboratory practices.

#### 4.1.2. Potential Contamination

During the course of a research cruise different steps are taken to insure that the chances for contamination are minimized. All containers used to collect bulk raw water are rinsed three times with sample (station) water before they are filled and are thoroughly cleaned with an acid wash and rinsed with deionized water and dried at the end of the cruise. All glassware associated with the preparation of standards and reagents is cleaned with deionized water and acid washed when appropriate.

Another area of potential contamination is the DATAFLOW system itself. Though we have never seen fouling or growth in the tubing, we do take measures to prevent any contamination. During each use, large volumes of water are pumped at a very high velocity through the system which prevents growth. After each use the intake, hoses and flow through cells are taken apart and allowed to dry completely and stored in the laboratory until they are reassembled for the next use. Periodically the components are rinsed with freshwater. The system is examined before each use for any fouling or growth.

### 4.1.3. Calibration Procedures and Frequency

All instruments (YSI 6600, YSI 6600 V2, YSI 600, and YSI 6920) are maintained in accordance with manufacturer's specifications. Sensors involved in the collection of water quality data (temperature, conductivity, salinity, pH, dissolved oxygen, turbidity, and chlorophyll) are calibrated just prior to each deployment. Standards and reagents involved in the calibration of instrumentation are made according to a schedule of shelf life (i.e. daily, weekly or seasonally) or if the supply is exhausted. All chemicals are handled, prepared and stored in accordance with standard laboratory practices. If any apparent problems arise the instrument is removed from use until the malfunction can be diagnosed and remedied.

The manufacturer calibrates temperature when the instrument is returned for service. The thermistor is also checked yearly against a NIST certified thermometer. For the Continuous Monitoring Program the Conductivity standard has a Specific Conductance of 10 mS/cm and is purchased from Fischer Scientific. For the Dataflow program a 0.2 molar standard solution of potassium chloride is made using DI water and Mallinckrodt Granular Potassium Chloride (FW 47.56) purchased from VWR. The solution is made by weighing out 29.82g of KCl (which has been dried and desiccated) using an analytical balance and adding it to a volumetric flask. The level of DI water is then brought up to 1000mL resulting in a standard of 24.82mS/cm. A 3-point calibration is used to calibrate the pH sensor, this includes a pH of 4.0, 7.0, and 10.0 (VWR Buffer Solutions). Dissolved oxygen calibration incorporates a standard air calibration based on air temperature and barometric pressure or for the Optical DO probe an air saturated water calibration technique. A 2-point calibration is used for calibration of the transmissometer (turbidity sensor): deionized water (0 NTU) and a YSI NTU turbidity standard at a level of 123 NTU. A 2-point calibration is also used for the

fluorometer: deionized water (0 ug/l) and an upper standard made with Rhodamine WT and deionized water (See Appendix C for more detailed information).

For transmittance and fluorescence, the manufacturer also recommends that the instrument be verified against in-situ properties measured in the field. This involves collecting verification samples during deployment that are analyzed for total and active chlorophyll-a and total suspended solids concentrations. These field standards are related to sensor readings via multiple regression procedures.

At all verification stations light attenuation measurements are taken using a Li-COR LI192SA sensor to relate to turbidity measurements gathered from YSI 6600 turbidity sensor as well as to the total suspended solid numbers.

**Quality of Verification Data** 

PARAMETER	UNITS	PRECISION	MDL	Method
PAR	μ mol/sec/m <sup>2</sup>	-	1 μ	LI-COR
			mol/sec/m <sup>2</sup>	190 <b>S</b> A
Light	-	1	0.5% @	Li-COR
Attenuation			100% light	192SA
Secchi Disk	m	1	0.1m	
TSS	mg/L	6 mg/L	2 mg/L	Gravimetric
Chlorophyll	μg/L	3.29µg/L	0.95 μg/L	Fluorescence

(See appendix D for more information on laboratory SOPs and methodologies)

# 4.1.3.1. Continuous Surface Water Quality Mapping (DATAFLOW)

### 4.1.3.1.1. Documents and Records

A cruise checklist is filled out prior to each cruise to ensure all field equipment is in order. A calibration sheet is filled out for both the YSI 600 and 6600 sondes. Data generated from the DATAFLOW System is continuously written to an ASCII text file on the hard disk of the unit. After each cruise the data is copied to backup disk as well as stored on the centrally managed VIMS shared file space that is backed up daily. Calibration station data are first recorded on data sheets, which are copied and stored with the Quality Assurance Officer, then transferred to electronic files, which are stored in an Access database. All field data and observations are recorded on specially prepared field data sheets. The initials of the person recording the data are recorded on each sheet. These sheets are filed with the Quality Assurance Officer. (See Appendix B for copies of all documents for field and lab data).

# 4.1.3.2. Fixed Station Water Quality Monitoring

#### 4.1.3.2.1. Documents and Records

A calibration sheet will be filled out for each YSI 6600 V2 as it is prepared to be placed out into the field. Verification samples and any information gathered during the retrieval/deployment process, including vertical profiles of dissolved oxygen, salinity and water temperature, are recorded on data sheets. These are initialed by the field personnel and filed by the Laboratory Supervisor.

## 4.2. Description of Individual Data Sets

# 4.2.1. Continuous Surface Water Quality Mapping (DATAFLOW) in the Rappahannock River System & the Virginia Embayments of the Potomac River

Two data sets contain the continuous surface water quality measurements.

-The sampling station field verification data set contains: date, time, latitude, longitude, total depth; concurrent instrument readings for temperature, specific conductivity, salinity, dissolved oxygen, pH, fluorescence, and turbidity; laboratory analyses for active chlorophyl1-a, total chlorophyl1-a, TSS, VSS, secchi depth, light attenuation and dissolved oxygen, water temperature, pH, and salinity for the vertical profile.

-The continuously measured DATAFLOW screened data set contains: date, time, depth, latitude, longitude for each record of water temperature, specific conductivity, salinity, dissolved oxygen, pH, chlorophyll and turbidity.

# 4.2.2. Fixed Station Water Quality Monitoring in the Rappahannock River System & the Virginia Embayments of the Potomac River

Two data sets are generated at the fixed stations.

-The sampling station field verification data set contains: date, time, latitude, longitude, total depth; concurrent instrument readings for temperature, salinity, dissolved oxygen, pH, fluorescence, and turbidity; laboratory analyses for active chlorophyl1-a, total chlorophyl1-a, TSS, VSS, secchi depth, light attenuation, and dissolved oxygen, water temperature, pH, and salinity for the vertical profile.

-The continuously measured data set contains: date, time, water temperature, salinity, dissolved oxygen, pH, chlorophyll, turbidity and depth values.

#### 4.3. General Information Related to Data Sets

# 4.3.1. Continuous Surface Water Quality Mapping (DATAFLOW)

#### 4.3.1.1. Raw Data Set Retrieval

The data are continuously transferred electronically from the YSI 6600 to the computer hard drive during each day of sampling. The data are stored as an ASCII text file. This file is retained indefinitely as the original record of the data collection. Upon completion of the cruise, data is retrieved from the Panasonic Toughbook laptop using a USB drive.

## 4.3.1.2. Initial QA/QC of Data Set

Very little post-processing is required before the data can be used. A macro has been developed that takes the raw downloaded dataflow text file and breaks it into columns, puts headers on the columns, changes the latitude and longitude to decimal degrees and highlights cells that have incorrectly formatted data (e.g. if there is text where there should be numbers). The data manager then looks over the data file, first focusing on the cells the macro has highlighted. The next step is comparing field notes to the data and highlighting areas of "bad" data (e.g. increased turbidity due to being too shallow while coming onto station or time spans of a clogged intake etc). Each parameter is then graphed to look for things such as single high spikes in the optical data that are questionable, strange trends in DO data (e.g. steadily decreasing levels that could indicate degradation in the electrolyte solution), or any other issues with probes that might appear in the data. These are all highlighted so that the associated error codes can be attributed to the data. Another step when dealing with both sets of data is to examine the YSI post calibration data and be sure that any drifts in the probes are within acceptable ranges. These ranges are listed in the table below. Once these checks have been accomplished, the data can be put into the final form for submission and the appropriate error codes are used to tag erroneous observations. (See Appendix E for a more detailed protocol for the processing of DATAFLOW data.)

Parameter	Value
Chlorophyll	$\pm 5$ % of true value
Dissolved Oxygen	±0.5 mg/L
PH	±0.2 pH units
Specific Conductance	±5 % of true value
Turbidity	±5 % of true value
Water Temperature	±0.2 °C

#### 4.3.1.3. Further Data Review

As indicated in section 3.1.6.1. of this document, project data is routinely monitored on a real-time basis for potential problems. Additional data reviews are conducted subsequent to the completion of the monitoring events as follows: As soon as the cruise is completed the Quality Assurance Officer/Data Manager downloads the raw data file and reviews the field documentation for legibility, accuracy, and completeness. Any issues are discussed with the field crew and the field sheets are initialed as being complete. Once reviewed the verification station information contained in the field sheets are transcribed onto an electronic version (Excel or ACCESS) and these files are subsequently examined for accuracy and completeness. The information contained on the electronic versions of the field sheets is then incorporated into the verification data database. Subsequent QA/QC of this dataset, as well as data analysis of the data by the Quality Assurance Officer (QAO) offers yet another opportunity to detect and correct any remaining errors which may have been over looked in the reviews and/or audits.

# 4.3.1.4 Comparisons Between DATAFLOW and Laboratory Derived Results

As previously described, the total chlorophyll values as determined by the YSI 6600 sondes can be corrected by results obtained in the laboratory as well as with turbidity values. The goodness of fit (measured as a regression  $R^2$  value) between laboratory derived chlorophyll a and corrected YSI will be statistically evaluated. Light attenuation (Kd) will be predicted by determining statistical relationships between YSI turbidity (NTU) and measured LiCor results (Kd) determined at the verification stations. The goodness of fit (measured as a regression  $R^2$  value) between LiCor measurements and YSI turbidity will be statistically evaluated.

# 4.3.1.5. Processing of Data

After the data is examined and coded, a final version is stored on the centrally managed VECOS database that is stored in VIMS shared file space and is backed up daily. The data is then imported into ArcMap and maps of the surface water quality conditions are produced using GIS software (ESRI ArcInfo). (See Appendix F for a more detailed GIS protocol to generate interpolations.)

## 4.3.2. Fixed Station Water Quality Monitoring

#### 4.3.2.1. Raw Data Set Retrieval

The data from the YSI 6600EDS V2 are uploaded to a Personal Computer (IBM compatible) upon return to the lab. Files are uploaded to a PC in a comma-delimited format. These are then backed up.

## 4.3.2.2. Initial QA/QC of Data Set

For the continuous monitoring stations, the data is downloaded into Ecowatch. In this program, graphs are created of each parameter and outliers are examined as well as any data trends which indicate trouble with individual probes. Depth data is compared with the rest of the data so that data can be tagged if the sonde was out of water and optical data is closely examined for periods where wipers may have seated over optics, etc. The same issues with the data/probes that are listed in the dataflow portion are examined in the continuous monitoring dataset. With the continuous monitoring stations, the dataset must also be joined to form a seamless file for the year's deployment. The times associated with any missing data are inserted and the appropriate error codes are placed in the cells to explain the absence of data. As with the Dataflow, YSI post calibration data is checked to be sure that any drifts in the probes are within acceptable ranges. Once these checks have been accomplished, the data can be put into the final form for submission and the appropriate error codes are used to tag erroneous observations. (For acceptable drifts see table above in section 4.3.1.2.) (See Appendix G for summary of QA for the Fixed Station data)

## 4.3.2.3. Processing of Data

Missing data due to YSI maintenance (down time) are inserted into the spreadsheet and are denoted by time stamps with no records. Edited files are merged to contain one full year of data for each station. Microsoft Excel macros provided by the NERR Centralized Data Management Office are used to discover data set outliers (values which fall outside the range that the instrument is designed to measure) and other erroneous data. Suspect data are evaluated, edited, and documented in each site's metadata document (data documentation)

# 4.4. Analytical Methods QA/QC

## 4.4.1 Analytical Services Center (ASC)

The Analytical Services Center (ASC) at VIMS provides water quality analyses to University, State and Federal agencies. As part of the laboratory's QA/QC program, ASC will participate in cross calibration exercises with other institutions and agencies whenever possible. Some examples include:

- -Quarterly cross calibration exercises with the Chesapeake Biological Laboratory (CBL) and Old Dominion University (ODU) in conjunction with the Chesapeake Bay Program's Coordinated Split Sample Program (CSSP).
- -Environmental Protection Agency (EPA) unknown audits for various nutrients have been conducted.

- -EPA audits of known nutrients were analyzed using samples in different salinity water while looking for possible matrix effects.
- -The Chesapeake Bay blind audit sample program which includes dissolved nutrients, particulate carbon, nitrogen and phosphorus, and chlorophyll.

As part of the Chesapeake Bay Tributary Monitoring Program, the laboratory analyzed approximately ten percent of the total sample load for QA/QC checks. These samples included laboratory duplicates and spike analyses.

### 4.4.2 "Bottle Blanks"

"Bottle Blanks" are necessary for the Whirlpak bags, which are used to collect sample filtrate in the field. Whirlpak bags are tested for contamination by selecting a number of bags (5) from each lot, filling them with deionized water, freezing them, and then analyzing the water for ammonium, nitrate, nitrite, and orthophosphate.

#### 4.4.3. Fluorescence Blanks

Fluorescence of dissolved organic matter (DOM) in natural waters can occur over the same wavelengths as chlorophyll, falsely elevating fluorescence readings of a YSI 6600 V2 Datasonde. The magnitude of this effect can vary both temporally and spatially. To quantify the magnitude of DOM fluorescence, subsurface (0.25m depth) water samples are collected at each fixed, shallow water monitoring station during the exchange of a YSI 6600EDS V2 sonde. The water is collected in a darkened bottle, brought back to the lab and allowed to sit overnight at room temperature. It is then filtered through a GFF, 0.7 µm pore size filter. The filtered water is collected and a newly calibrated YSI 6600 is used to determine the fluorescence of the water using a 6025, YSI chlorophyll probe. This number is then recorded and may be used in the future to correct fluorescence readings.

## 4.4.4. Sample Custody

Upon arrival at the laboratory, samples are counted, observed for potential problems (melting, broken containers, etc.), processed, and placed in a freezer until analysis. Sample information and date of arrival, times of filtering and storage by freezing are recorded on a log sheet.

#### 4.4.5. Instrument Maintenance

Analytical instruments are maintained on a regular basis and records are kept of hours of operation, scheduled maintenance, pump tube changes, etc. A critical spare parts inventory is maintained for each instrument. Instrument down time is minimized by troubleshooting instrument problems telephonically with manufacturers and service representatives. Spare

parts can be received within 24 hours via next-day air service. Backup YSI 6600EDS V2 sondes are also maintained as backup instruments.

## 4.4.6. Data Handling

Data are entered in a pre-determined format in an Access Database on a computer. Any necessary corrections are noted and made. Any data errors are given specific error codes. All data are backed up on tape on VIMS server. Specific data handling procedures are provided above and will be provided in the data management protocol.

## 4.4.7. Data Analysis

Preliminary data analysis is performed in which data from the DATAFLOW system is interpolated over 25m cells for the given study sites using kriging techniques with the software package Geostatistical Analyst. This data is served, as interim data, on the program website www.vecos.org.

The primary purposes for these data collection are for assessment of attainment of water quality standards (see Appendix F for a detailed methodology of water clarity analysis). Data analyses will determine attainment/non-attainment of numerical standards for water clarity in the CBP segments being monitored by VIMS. Data to be used include those collected by VIMS as well as other data appropriate to the purpose (e.g. HRSD Monitoring data). Protocols used will be those published in EPA or DEQ guidance or otherwise as determined by the CBP Criteria Assessment protocols workgroup, EPA CBP Office, or DEQ with the advice and expertise of VIMS. Below is a general outline of data analysis tasks to be completed. Some tasks will be joint efforts among staff from DEQ, VIMS, and EPA-CBPO as appropriate and capable.

# 1) Rappahannock River

Migratory and Spawning Designated Use

# Dissolved Oxygen

- Assessment of the special representativeness of each fixed station (including vertical profiler).
- Assessment of attainment of appropriate criteria.
- Spatial Interpolation of data.

Shallow Water Designated Use

#### Water Clarity

- Assessment of SAV acres criteria based on annual SAV surveys.

 Assessment of "Water Clarity Acres" criteria based on combined DATAFLOW data and SAV surveys.

# Open Water Designated Use

# Dissolved Oxygen

- Assessment of appropriate criteria based on DATAFLOW verification stations, DEQ tributary monitoring data, volunteer monitoring data.
- Spatial Interpolation of data.
- Assessment of D.O. Criteria based on fixed site CONMON data.
- Assessment of the representativeness of each fixed station (including vertical profiler).

# Deep Water Designated Use

## Dissolved Oxygen

- Assessment of appropriate criteria based on DATAFLOW verification stations and DEQ tributary monitoring data.
- Spatial Interpolation of data.
- Assessment of appropriate criteria based on vertical profiling CONMON data
- Assessment of the spatial representativeness of the CONMON vertical profiler.

## Deep Channel Designated Use

## Dissolved Oxygen

- Assessment of appropriate criteria based on vertical profiling CONMON data
- Assessment of the spatial representativeness of the CONMON vertical profiler.

# 2) Potomac River

## Shallow Water Designated Use

#### Water Clarity

- Assessment of SAV acres criteria based on annual SAV surveys.
- Assessment of "Water Clarity Acres" criteria based on combined DATAFLOW data and SAV surveys.

## Open Water Designated Use

## Dissolved Oxygen

- Assessment of appropriate criteria based on DATAFLOW verification stations, DEQ tributary monitoring data, volunteer monitoring data.
- Spatial Interpolation of data.
- Assessment of D.O. Criteria based on fixed site CONMON data.
- Assessment of the representativeness of each fixed station (including vertical profiler).

#### 4.4.8. Data Submission

Data will be formatted according to EPA standards and protocols. As QAQC on the data is completed it will be uploaded to a database and made available for download by EPA through a webservice. While data can be downloaded as it is ready, final data submission for all associated data and metadata to the Chesapeake Bay Computer Center (CBCC) is March 30, 2010 for 2009 data. FGDC compliant CIMS Level 3 metadata will also be submitted at the time of data submission. Data is also available in graphic format and interpolated maps to the public at www.vecos.org. Both Continuous data and DATAFLOW data can also be downloaded from this site.

#### 4.5. Field Audits

The Quality Assurance Officer (QAO) will perform audits of field procedures at a frequency of once per season (Spring and Summer). These field audits will consist of the following elements.

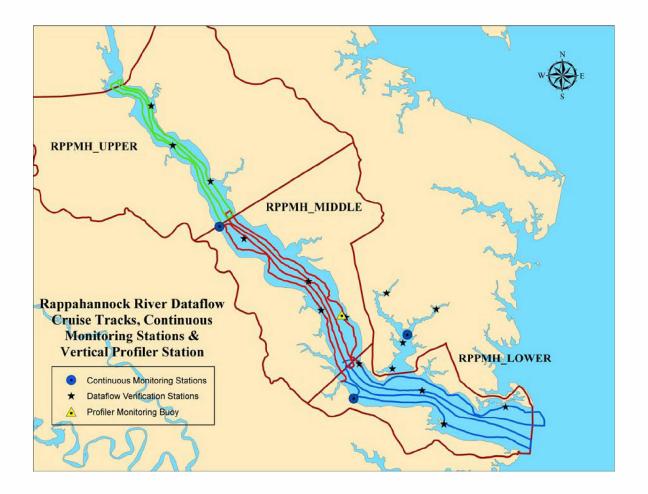
- The QAO will accompany the field crew during selected sampling events. The methods employed by the crew will be compared to those described in this project goals document.
- The QAO will review the QA/QC measures described in this section relative to project goals. To assist this process the Project Manger will provide the QAO with the results of data analyses related to goodness of fit relationships, field duplicates, and field blanks described in this section.
- The QAO will review the project files, documentation, and QA/QC data set for completeness and accuracy.
- The QAO will develop a summary report of findings and report them to the Project Manager.
- The Project Manager will address the issues identified by the QAO in the field audit process.

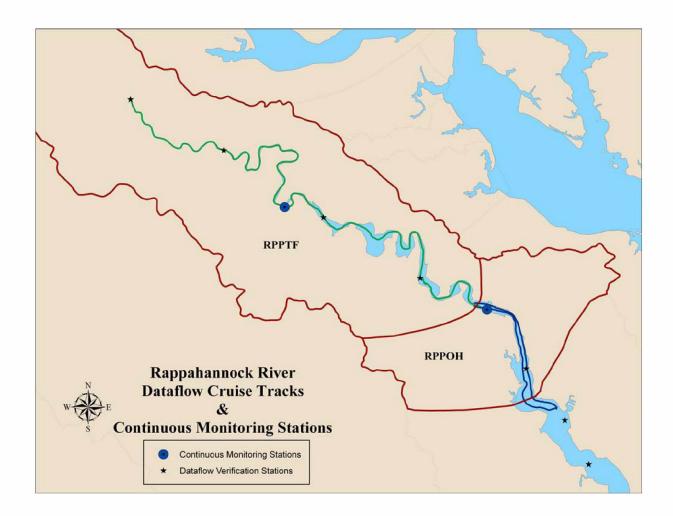
#### 4.6. Schedule of Deliverables

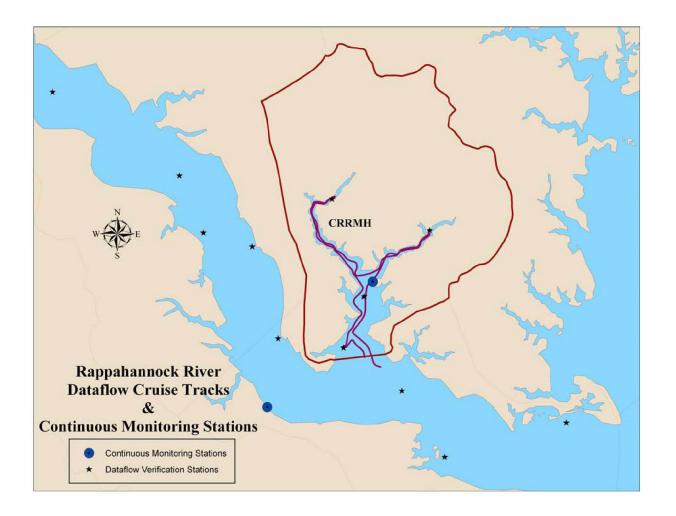
PROGRESS REPORTS: Semi-annual status reports will be submitted at the general beginning and end of each field season per below schedule. These reports will contain the following sections: Summary Statement; Conformance to Sample Collection and Analysis Goals; Data Submittal Status; Quality Assurance/Quality Control Status; Statement of Work Planned for Next Reporting Period.

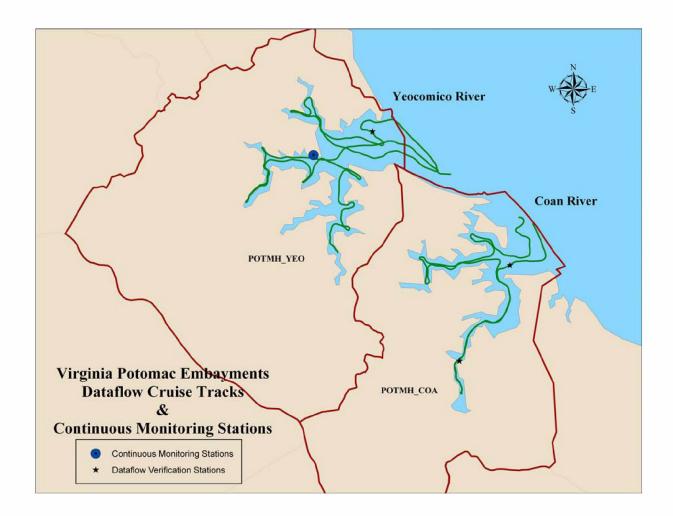
Status Report for 1/2009 - 6/2009 7/5/2009 Status Report for 7/2009 - 12/2009 1/15/2010

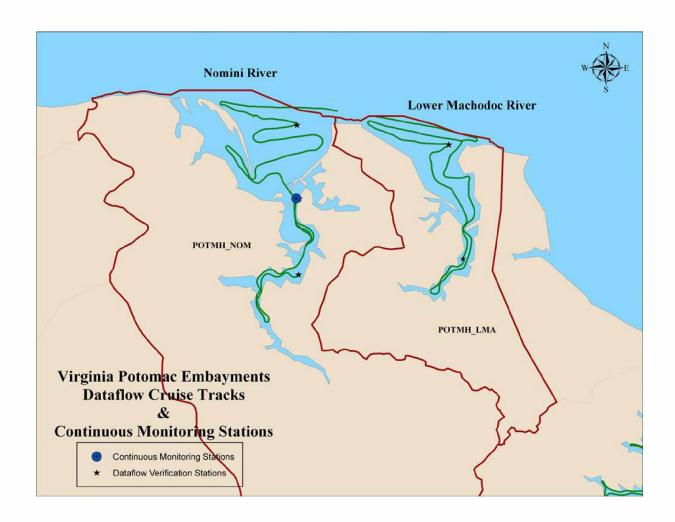
# Appendix A: Map of Study Site Locations

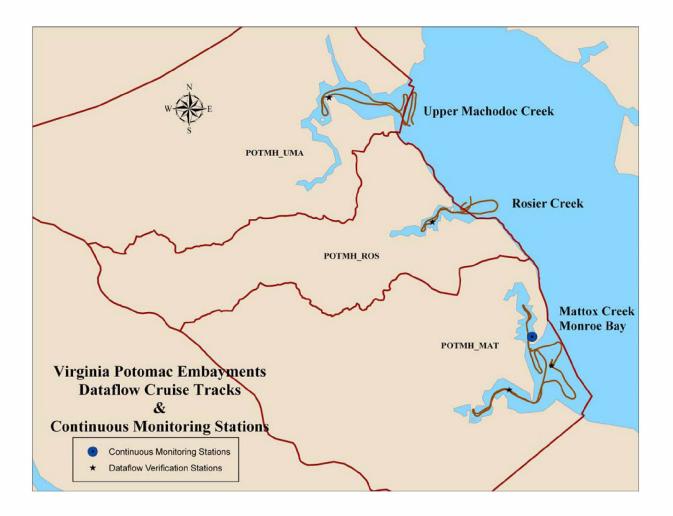


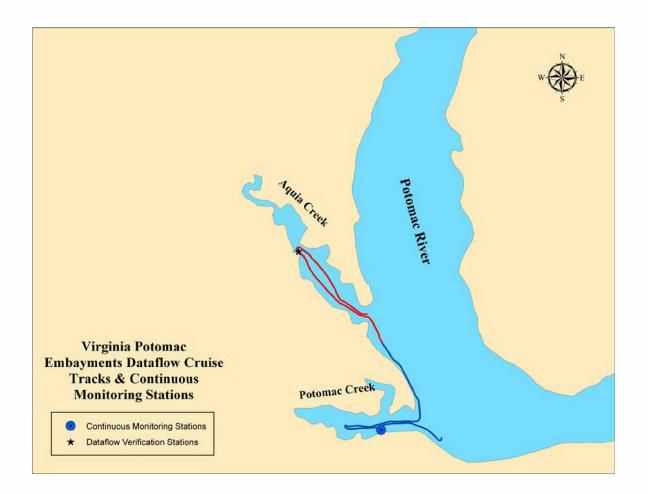












Appendix B: Examples of calibration worksheets, field checklist, and field datasheets.

# Calibration Work Sheet – Dataflow

Date of Calibration:	Technician:			
DO membrane changed? Y N Note:	Wait 6-8 hours before final DO cali	bration.		
Turbidity wiper changed? Y N	Wiper Parks $\approx 180^{\circ}$ from opt	ics? Y N		
Chlorophyll wiper changed? Y N	Wiper Parks $\approx 180^{\circ}$ from opt	ics? Y N		
Record Battery:				
DO Warmup <u>60sec</u> Y N Wiper	r Interval <u>15</u> Y N RS232 Sleep <u>D</u>	Disabled Y N		
<b>Record Calibration Va</b> Actual Sond	Alues Record diagnostice after cal	cs <u>after</u> calibration.		
Conductivity	Conductivity constant	Range 5.0 ±.5		
pH (mid)	pH MV mid buffer	Range +180 ±50		
pH (high)	pH MV High buffer	Range -180 ±50		
	Span between the 7 and	10 MV numbers should be		
Turbidity (0)	$\approx 170 - 180 \text{ M}$	V.		
Turbidity (123)	(if post cal # for 0 turbic	dity is $> +/- 2.0$ see manual!)		
Chlorophyll (0)				
Chlorophyll (100)	DO Charge	Range 50 ±25		
Dissolved Oxygen	DO Gain	Range 1.03 to +.4		
Barometric Pressure		ow electrolyte or tear Oxidation of probe		
DO Calibration Hi/Lo Transmission Te	est Accept	Reject		
Morning of Deployment				
Dissolved Oxygen	DO Charge	Range 50 ±25		
Barometric Pressure	DO Gain	Range 1.03 to +.4		
Proper parameters selected in Report Men Time, Temp (C), SpCond (mS/cm), Sal (p Battery (v)		lity (NTU), Chlorophyll (mg/l		
Post Calibration: Conductivity (24.82): Chlorophyll (0):	pH (6.86): Battery:	Turbidity (0):		
DO (precal): If any parameter has drifted can do a more	Battery: DO (postcal): e indepth post cal (eg high and low s	Barometer:		
	o macpui post out (og mgn and low s	minding for City 1 tito.		
Notes:		Revised 4-25-03		

# Rappahannock River Cruise Check List

Cruise Date:			
Dataflow Opera	ator:		
Discolund Ovygon/LaMotto Kit		Clipboard	
Dissolved Oxygen/LaMotte Kit Sample Bottles		Sample Protocols	
LaMotte Kit		Field Data Sheets	
DI Water Rinse Bottle		DO Profile Data Sheets	
		Kestrel Handheld	
Filtration Kit		Pencils	
Whirlpak Bags - Chlorophyll		Sharpies	
5ml Pipette		·	<u></u>
Pipette Tips		Computer Equipment	
Vacuum Hand Pump		Toughbook Computer (TB2 or TB3)	
Receptacle Flask		TB2 or TB3 Container	
Chlorophyll Chimney		Powercord	
Chlorophyll Frit		Dual Serial Cord	
Chlorophyll Clamp		GPS to Computer Cable	
Filter Forceps (2)		Wireless Modem (optional)	
Foil for Chlorophyll Filters		Computer Cig Lighter Adapter	
Chlorophyll Filters			
DI Rinse Squirt Bottle		Dataflow Equipment	·
Kim-wipes		YSI to Computer Cable	
Sharpie		YSI 6600	
Extra Whirlpaks		YSI 6600 Backup	
Trash Bin		YSI 600 w/handheld (long cable)	
Ziploc Bags for Samples		Flow through Cell	
		Intake Hose	
Sample Coolers		Effluent Hose	
Large Sample Cooler		Hose Clamps 3)	
Small Sample Cooler		Bungee Cords	
Large Nalgene Sample Bottles		Ram Intake with Pump	
Small Nalgene Sample Bottles		Spare Pump	
Large Nalgene with DI Water		Bucket	
Ice		Spare PVC Intakes	
Linkt Attornation Kit			
Light Attenuation Kit		Other essentials	
Datalogger		Spare Batteries	
Deck Sensor Underwater Pole/Sensor	$\vdash$	Spare DO Flatter to	
Secchi Disk		Spare DO Electrolyte	
Secon Disk		Spare fuses	
		Toolbox	
		Towels	
		47	

# Shallow Water Monitoring – Dataflow Field Sheet

Date:	Cruise Location: Potomac Embayments
Personnel:	
	Nest Point, East side (garage w/ green roof)
Sample Time: DF 6600 ID:	Sample Bottle #: <u>POTMH 1</u>
Computer File Name (s):	
DF 6600 Data (on station):	YSI-600 ID #for Verification:
Time (on DF): _	
Dissolved Oxygen (%):	Dissolved Oxygen (%):
Dissolved Oxygen (mg/l):	= 15501, <b>cu</b> 011, 8 <b>c</b> 11 (111, 611).
Water Temperature:	Water Temperature:
Salinity:	Salinity:
pH:	pH:
Turbidity	
Chlorophyll	
Station Conditions:	Other Data:
Station Depth:	Secchi Depth:
Air Temp:	Light Attenuation Time:
Wind Speed (m/s):	Chl Amt Filter:
Wind Direction:	
Cloud Cover (0-6):	Make Note of Agreement btw 6600/600:
Wave Condition (0-5):	D.O. should be within 0.5 mg/l
Precipitation Type (10-16):	pH should be within 0.4 ppt
Tide Stage (E, F, H, L):	Temperature should be within 0.25 degrees
Comments:	
<u>'</u>	
DF 6600 (averages - lab use only):	
Latitude:	Data entered/edited by
Longitude:	
Depth:	
Water Temp:	
Salinity:	
pH:	
Dissolved Oxygen (%):	
Dissolved Oxygen (mg/l):	
Turbidity:	
Chlorophyll:	Revised 4/3/09

Data Lagger ID:	WQ Initiative YSI 6600-V2 ROX CA	LIDKATION, DEFI	LOYMENT+RETRIEVAL	LOG	
Date (MM/DD/YY):	RIVER SYSTEM: Time correct (EST): YES	S NO			
Version:	Sonde Serial Number:	Calibrated l	Ву:		
Conductivity Probe ID:	pH probe ID:	Optical DO I	Probe ID:		
Turb. Probe ID:	Chlorophyll probe ID:	OTHER ID:			
Battery Volts:	Changed batteries?: YES NO				
	ed: Y N; Wiper parks ~180° from or				
Chlorophyll Wiper Cha	nged: Y N; Wiper parks ~180° from op nged: Y N; Wiper Parks ~180° from o				
Calibration: (enter standard		pues: 1 N			
Spec. Cond.:					
pH 7:	error message:				
pH 10 :	error message:				
pH 4 ·	error message:				
Turbidity: (0)	(123) error message: (Depth Offset: (mmHg):				
Depth :	(Depth Offset: (mmHg):	_ =(m))	cal'd to:		
*ROX DO%:	/**Temp	erature stabilized?	Yes No		
Barometric press: (mm I.	////_**Temp	millibars)			
Date and time recorded.		(%)			
Conductivity Cell Constant	nostic numbers after calibration:	6 to 5.45)			
DO Gain	(range 0.8 to 1.7)	0 10 .7.4.7)			
pH MV Buffer 7	(range 0.6 to 1.7)	mv + 50 mv) SI	ope→ mV(7) - mV(10)=_		
pH MV Buffer 10	(range o	80  mv + 50  mv	(should be 16	55-180)	
pH MV Buffer 4	(range +:	180 mv ± 50 mv)	(Bhoma be 10	2-100)	
Notes:					
Programming:					
	ES NO Disk Free Space:				
Parameters: date, time, tem	p (C), SpCond (mS/cm), Sal (ppt), DOSAT%,	DO (mg/L), Depth (	m), pH, Turb (NTU), Batt		
Datalogger FILENAME (S	SSyymmdd):				
	- CI I I II III II		Verification	Deploy	Retrieve
	Chlorophyll calibration		Sample	DL#	DL#
	2 pt calibration using Rhodamine WT		DO mg/L		
			Mini %	<u> </u>	
		1	l		
DI water	Temp of solution	ug/L	Mini mg/L		
	Temp of solution	μg/L	Mini mg/L Temp A	<u> </u>	
DI water (0)	Temp of solution	μg/L	Temp A		
	Temp of solution	μg/L	Temp A		
	Temp of solution	μg/L	Temp A	cm	cm
		μg/L	Temp A  W  Turb/secchi	cm	cm
	Temp of solution  Output  Output  Description:  Output  Descriptio	μg/L	Temp A		
		µg/L	Temp A  W  Turb/secchi  Salinity	cm	cm
		µg/L	Temp A  W  Turb/secchi		
		μg/L	Temp A  W  Turb/secchi  Salinity		
		µg/L	Temp A  W  Turb/secchi  Salinity		
		µg/L	Temp A  W  Turb/secchi  Salinity		
		µg/L	Temp A  W  Turb/secchi  Salinity		
		µg/L	Temp A  W  Turb/secchi  Salinity		
(0)		µg/L	Temp A  W  Turb/secchi  Salinity		
days		µg/L	Temp A  W  Turb/secchi  Salinity		
nemory days		µg/L	Temp A  W  Turb/secchi  Salinity		
nemory days y life days ing interval: 15 - minute		µg/L	Temp A  W  Turb/secchi  Salinity		
nemory days		µg/L	Temp A  W  Turb/secchi  Salinity		
nemory days y life days ing interval: 15 - minute ing duration: "365 days"		µg/L	Temp A  W  Turb/secchi  Salinity	ppt	ppt
nemory days y life days ing interval: 15 - minute	° C =μg/L]	µg/L	Temp A  W Turb/secchi  Salinity  pH		ppt
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days days ing interval: 15 - minute ing duration: "365 days"  Date (mm/dd/yy):/_ Start Time (HH:MN or Mark)	° C =µg/L]:(:14:29:44:59):Time (HH:MM, LST)::TIDE: Flood, Ebb, Slack_H		Temp A  W Turb/secchi Salinity pH	ppt  Checked Logging  Iold (CO,): □	ppt
days y life - days ing interval: 15 - minute ing duration: "365 days"  Date (mm/dd/yy):/_ Start Time (HH:MN  Degger Deployment: SIT  mm/dd/yy):/_ /	° C =µg/L]:(:14:29:44:59):Time (HH:MM, LST)::TIDE: Flood, Ebb, Slack_H		Temp A  W Turb/secchi Salinity pH	ppt  Checked Logging  Iold (CO,): □	ppt
days varies and the more of th	° C =µg/L]:(:14:29:44:59):Time (HH:MM, LST)::TIDE: Flood, Ebb, Slack_H		Temp A  W Turb/secchi Salinity pH	ppt  Checked Logging  Iold (CO,): □	ppt
days y life days y life days ing interval: 15 - minute ing duration: "365 days"  Date (mm/dd/yy):/_ Start Time (HH:MN  ogger Deployment:/ er: current wind spd  ogger Retrieval:			Temp A  W Turb/secchi Salinity pH	ppt  Checked Logging  Iold (CO,): □	ppt
days days ing interval: 15 - minute ing duration: "365 days"  Date (mm/dd/yy):/_ Start Time (HH:MN  Deger Deployment: mm/dd/yy):/_ er:current wind spd  Deger Retrieval:		igh, Slack_Low	Temp A  W Turb/secchi Salinity pH	ppt  Checked Logging  Iold (CO,): □	ppt
days y life days y life days y life days y life days Thing interval: 15 - minute ing duration: "365 days"  Date (mm/dd/yy): / Start Time (HH:MN Deger Deployment: Minute (HH:MN Deger Retrieval: Minute (HH:MN Dege		igh, Slack_Low	Temp A  W Turb/secchi Salinity pH	ppt  Checked Logging  Iold (CO,): □	ppt
days days ing interval: 15 - minute ing duration: "365 days"  Date (mm/dd/yy):/_ Start Time (HH:MN  Deger Deployment: mm/dd/yy):/_ er:current wind spd  Deger Retrieval:		igh, Slack_Low	Temp A  W Turb/secchi Salinity pH	ppt  Checked Logging  Iold (CO,): □	ppt
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days y life days y life days y life days y life days Thing interval: 15 - minute ing duration: "365 days"  Date (mm/dd/yy): / Start Time (HH:MN Deger Deployment: Minute (HH:MN Deger Retrieval: Minute (HH:MN Dege		igh, Slack_Low	Temp A  W Turb/secchi Salinity pH	ppt  Checked Logging  Iold (CO,): □	ppt

Post Deployment Calibra	ation Check:	SONDE ID:_			
Post Calibrated by: Date :			Time correct:		
		•			
FILE NAME:	dat	txt			
Sp Cond:	Cond Cell Consta	nt: (r	ange 4.6 to 5.45)		
pH 7: pH mv _	(range 0 mv ± 50 m	v)	*Clean Sonde Filtrate	<u>:</u>	
pH 10: pH mv _	(range -180 mv <u>+</u> 50	mv)	CHL : μg/I		
pH 4 : pH mv _	(range +180 mv <u>+</u> 50	) mv)	RFU/FS: %	, O	
Turbidity [0]:	Turbidity (123)	):			
CHL [0]:		(Chl temp (	<u> </u>	ug/L)	
DEPTH : =		CHL [	]: reading	μg/L	
ROX % DO :	% DO GAIN:				
DO NOTES:					
Barometric Pressure (mn Time/Date recorded:	nHg)=		= ~theoretical sat'n DO]		
Wipers park:	TurbChla	ODO	other		
Wipers changed :	_Turb Chla	ODO	other		
	Changed Batteries:				
FIELD NOTES:					
	oling using MINISONDE @ 0				

WATER QUALITY MONITORING DEPLOYMENT AND RETRIEVAL LOG
CBNERR-FIELD-FRM-YSI DEPLOYMENT AND RETRIEVAL LOG

	mm	dd	уу
DATE			

Field Location		Crew	
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DATALOGGER INFORMATION		
	YSI ID Number	Time (EST)
Deployment (in)	YSI ID Number	Time (EST)

			WEATHER INFOR	MATION		
	Weather Conditions measured with Kestrel		Wind S	peed		Cloud Cover
Comment Wind C	- and ((a)		0 0-1 (knots)	0-1 (m/s)	0	Clear (0-10%)
Current Wind S	peed (m/s)	1 >1 - 10 1-5		1	Scatter/partly Cloudy (10-50%)	
Air Town (C)			2 >10 - 20	5-10	2	Partly to Broken (50-90%)
Air Temp (C)			3 >20 - 30	10-15	3	Overcast (>90%)
Relative Humid	ite: (9/)		4 >30 - 40	15-21	4	Foggy
Relative mullio	inty (%)		5 > 40	21-26	5	Hazy
					6	Cloud (no percentages)
	Precipitation Type			Wind	Direction	
10	None	E	fr East (90 deg)		S	fr South (180 deg)
11	Drizzle	ENE	fr East NE (67.5 deg	3)	SE	fr SE (135 deg)
12	Light Rain	ESE	fr East SE (112.5 de	g)	SSE	fr South SE (157.5 deg)
13	Heavy Rain	N	fr North (0 deg)		SSW	fr South SW (202.5 deg)
14	Squally	NE	fr NE (45 deg)		SW	fr SW (225 deg)
15	Frozen Precipitation	NNE	fr North NE (22.5 d	eg)	W	fr West (270 deg)
16	Mixed Rain&Snow	NNW	fr North NW (337.5	deg)	WNW	fr West NW (292.5 deg)
		NW	fr NW (315 deg)		WSW	fr West SW (247.5 deg)
			WATER INFORM	IATION		
W	ater and Secchi Depths	W	ave Heights	Tidal	Stage	VERIFICATION SAMPLES
Water Depth	(m)	0	0 < 0.1m	(circle one)		Chla Filter Volume
water Depti	1 (111)	1	0.1 < 0.3m	Е	Ebb Tide	·
Secchi Depth (r	m)	2	0.3 < 0.6m	F	Flood Tide	
secom Depui (i	11)	3	0.6 < 1.0m	Н	High Tide	
Circle if secchi	can be SD>= WD	4	1.0 <1.3m	L	Low Tide	
seen at bottom		5	>1.3m			

ATER COLUMN						
Depth m	Temperature	SpCond	Salinity	DO(%Sat)	DO(mg/l)	pН
0.10						
0.25						
0.50	Ī					
0.75						
1.00						
1.25						
1.50						
1.75						
2.00						
2.25						
2.50						

Please circle Minisonde used today:  $\ \#1\ \#2\ \#3$ 

COMMENTS:

2000	VIMS	OADI

Appendix C: YSI 6-series Multiparameter Water Quality Monitoring Standard Operating Procedure

#### INTRODUCTION

This document outlines the standard operating procedures (SOP) for the collection of data using YSI 6600 series Multi-Parameter Water Quality Monitors (sondes). The CONMON and vertical profiling stations utilize the ROX optical dissolved oxygen probes (YSI 6600EDS V2) while the DATAFLOW mapping system utilizes the Rapid Pulse dissolved oxygen probes (YSI 6600), therefore different calibration procedures are used. Calibration procedures for all other parameters are identical.

#### I. PREDEPLOYMENT

Before the instrument can be deployed it must be calibrated and several maintenance steps performed. The instrument should be visually inspected for any abnormalities, such as a cracked pH probe or cracked bulkhead. A <u>YSI 6-Series Lab Calibration</u>, <u>Deployment</u>, <u>and Retrieval Log</u> must be completed for each instrument calibration, deployment, and retrieval procedures (Appendix B).

#### **I.A: Probe Calibration Procedures:**

During the calibration of the probes **NEVER** accept any calibrations that you have been given a warning message on. You must determine the cause of the problem, correct the problem, and recalibrate the probe before deploying the instrument. Standards must be active (check expiration date) and fresh for all calibrations. Previously used standards may be used to rinse probes but must not be used to calibrate. Discard and replace all expired standards.

Calibrations should only be done with a PC (e.g., desktop, laptop, palmtop). The DM610 will automatically accept the turbidity calibration which can lead to a calibration corruption (see section I.A.6). Therefore the DM610 should only be used to transfer or collect data.

Most system diagnostic parameters (e.g., DO charge, ISE charge, conductivity cell constant are found in the "Cal-Constant" menu which you get to by selecting "Advanced" on the "Main" menu.

<u>I.A. 1.a.</u> Dissolved Oxygen Calibration for YSI 6600 Rapid Pulse type sensor (DATAFLOW)

The dissolved oxygen membranes are to be replaced before <u>each</u> deployment. The oxygen probe needs to rest for a minimum of 6 hours (12 hours is optimal) after the membrane is changed to allow the probe to stabilize electro-chemically. Calibration must be done in the following order:

- 1. Replace DO membrane;
- 2. Place probe (or sonde) in calibration cup with a wet sponge and let rest for 6-12 hours;
- 3. After 6-12 hours, run instrument in discrete sample mode until the DO % reading stabilizes. If the DO probe is working correctly, the past 24 numbers (one screen width) should be the same indicating the probe has stabilized (do not

- worry about the actual number, you have not calibrated the probe yet);
- 4. Calibrate the DO sensor following YSI's instructions for 100% air saturation calibrations.
- 5. Check the DO charge and gain. The DO gain is in the "Cal-constants" screen; the DO charge must be added to the report menu (remember to remove this from the report menu prior to programming). DO charge should be in the range of 25-75 counts. Counts below this range indicate low electrolyte or a tear in the membrane and counts above may be due to oxidation of the electrodes.
- 6. Perform a high/low transmission test. Start another discrete sampling. If the %saturation is at or above 100% and then drifts down (or slightly up) to 100%, the probe is functioning properly. If the %saturation is very low or negative and then climbs to 100%, the probe is failing due to reverse polarity of the electrodes. If this happens, the probe is either in dire need of a reconditioning or will need to be replaced. Record either pass/fail on tracking sheet. **Do not deploy the probe if it fails this test. The data will not be valid.**

#### I.A.1.b.: YSI Alternate method

The above protocol (I.A.1.a.) is sufficient for collecting data at the accuracy we are striving for and will also identify a faulty probe. The benefits of this alternate method are to: 1) provide additional time to identify a faulty probe prior to deployment; 2) allow a greater stability to the DO probe; and 3) provide additional data prior to deployment (6 to 12 hours of data) which can aid in the determination of the cause of invalid data.

Calibration procedures must be done in the following order:

- 1. Replace the DO membrane;
- 2. Place the sonde in the calibration cup with a wet sponge and wait five minutes. Calibrate the DO sensor. After calibration confirm that the charge, gain, and high/low transition tests pass (see section I.A.1.a). Record diagnostic numbers on the tracking sheet. NOTE: this is only a DO calibration check, the final probe calibration will be completed after the probe rests with the new membrane for 6 to 12 hours;
- 3. Calibrate pH (I.A.4);
- 4. Calibrate depth (I.A.2);
- 5. Calibrate conductivity (I.A.5);
- 6. Calibrate turbidity (I.A.6);
- 7. Calibrate chlorophyll (I.A.7);
- 8. After calibration is completed, begin the unattended sampling for 6 to 12 hours before deployment. This will allow the DO probe to stabilize. Just prior to deployment, calibrate the DO probe one last time (this can be done with the sonde still in unattended mode). Do not run the sonde in discrete mode for 12 hours as an alternative. The pre-deployment data that will now be in the data record will be a valuable tool to identify problems encountered during deployment.

# <u>I.A.1.c.</u>: Dissolved Oxygen Calibration for YSI 6600EDS V2 ROX Optical type sensor (CONMON and Vertical Profilers)

- 1. Aerate a 5 gallon bucket <sup>3</sup>/<sub>4</sub> filled with tap water for at least 1 hour prior to calibrating the Optical D.O. probe. This will create an air-saturated water environment (hereafter referred to as a 100% air-saturated water bath).
- 2. Place the sonde in the bucket (with pump still running) for at least 15-20 minutes in order to achieve temperature stabilization. Ensure that air bubbles are not streaming directly towards the Optical D.O. probe face. Warning: The membrane on the ROX DO probe MUST be kept hydrated in either water saturated air or immersed in water when not is use. If the membrane is allowed to dry out it will need to be hydrated per the instructions in the YSI manual.
- 3. Check the sonde (in discrete mode) to ensure temperature stabilization has occurred. Note: The ROX DO does not have a burn-in period and can be used in Discrete or Unattended applications with the same calibration. No DO warm-up or Auto-Sleep settings are required.
- 4. Begin the Optical D.O. Probe calibration
- 5. Choose "1-point calibration".
- 6. Enter the barometric pressure when prompted and continue calibrating. Record the DO gain just as you would with the rapid pulse probe. *NOTE: There is no DO charge option for this probe.*
- 7. Return the sonde to the 100% air-saturated water bath upon completion of all calibrations.
- 8. Place the sonde in unattended sampling mode at the normal 15 minute interval.
- 9. Leave the sonde in the air-saturated water bath until deployment.
- 10. At deployment time, check the D.O. value (DO %) to ensure the probe is reading accurately. The true reading that the probe should be showing is calculated using the following equation:

BP/7.6 = % Saturation Value (BP = current barometric pressure in mmHG)

- 11. The calculated and measured DO readings must agree within 1% before deployment. If they do not, the probe can be recalibrated while still in Unattended mode. Some drift can occur after the initial calibration if the membrane was not fully hydrated.
- 12. The probe's membrane requires annual replacement and is performed by unfastening the flat head screws located on the probe face. Please follow all directions that came with the probe provided by YSI.

# I.A.2: Depth/Pressure

The depth sensor is calibrated to sea level or level of the laboratory. **CAUTION:** When calibrating the <u>6600 with vented depth</u> you must use a vented cable during the calibration procedure. Failure to do so will result in a 3-4 meter shift in the water depth.

## <u>I.A.3</u>: Temperature

The temperature probe does not require calibration.

# <u>I.A.4:</u> pH

Check the ISE charge (pH mV) before calibration:

pH mV must be added to the report menu then run discrete sampling. Remember to remove pH mV from report before programming.

The ISE charge (pH mV) in pH 4 is 180 ±40mV, in pH 7 is 0 ±40mV and pH 10 is -180 ±40mV. Analog voltages above or below may indicate a problem with the sensor or the sonde. Note the diagnostic milli-volt numbers on tracking sheet. Note the span between the 7 and 10 pH milli-volt numbers and confirm that all meet specifications.

Buffer solutions of pH 7, 10, (or 4 depending on anticipated range of pH measurements) for the two point pH calibration are purchased pre-made from a scientific supply house. Old solutions can be used for rinsing probes, but guard against cross contamination of solutions. The pH calibration solutions are certified at a temperature of 25°C (see bottle label), and calibrations far outside of this range should be avoided.

# <u>I.A.5</u>: Salinity and/or Conductivity

The salinity and conductivity standards are obtained from filtered seawater taken from the local area and analyzed using an osmometer (or counter top meter) OR should be purchased from a

chemical supply company. After a correct calibration, the conductivity cell constants should be 4.6 - 5.45 as seen in the "Diagnostics" or "Cal-Constants" screen. Also note any change between the last calibration and the cell constant of the most recent. A probe that suddenly goes out of range usually means that either the standard used was contaminated, the probe had a trapped air bubble, or not enough standard was used to cover the vent hole on the side of the sensor.

### I.A.6: Turbidity

**Do not use plastic beakers or opaque plastics for this calibration**. Best results are obtained using **glass beakers** where you can see into the standard and watch for air bubbles near the optics and also check to make sure the wiper parks 180° from the optics. The probe face must be kept a minimum of 1 inch from the container bottom. Calibrations should also only be done over a **flat black surface since glare can interfere with the probe reading.** 

Carefully check the set screw on the turbidity wiper block for tightness and inspect wiper sponge for wear and color (the wiper should be white). It is recommended that the wiper be changed before all deployments. For turbidity, the calibration software setting should be 1 wipe (the default) every five minutes, but may need to be increased depending on fouling. The averaging interval for turbidity should be the default of 8. For DATAFLOW a wipe should occur every fifteen minutes. The turbidity calibration solutions are purchased at 100, 200, 800, or 1000 NTU concentrations (other NTU standards can be special ordered). Two-point turbidity calibrations may not be needed at every deployment and all should only be performed in the lab. YSI recommends that the two-point calibration only be done once a month (or when drift is evident). Low end (0.0 NTU) calibrations are the most critical and must be done for every deployment.

CAUTION: It is possible to corrupt the internal turbidity calibration constant of the instrument. Once this is done, slightly negative or positive values will be recorded for 0.0 NTU (greater than +/- 2.0 NTU). This corruption occurs when either the probe is not clean, an air bubble intercepts the light beam, or the 0.0 NTU standard is contaminated when you accept the calibration for 0.0 NTU. Care is therefore essential to insure the standard is clean and nothing is interfering with the probe (hence the need to use clear glass when calibrating turbidity). Once the calibration constant has been corrupted, you will need to contact YSI to reset (the YSI technician can walk you through the procedure). Until this is done, all future calibrations will be inaccurate and all turbidity data collected will be erroneous. In the PC environment you are given a choice to accept the calibration, however, using the DM610 you are not given this acceptance step so it is easier to cause this internal corruption problem when calibrating turbidity with the DM610.

<u>CAUTION:</u> Never accept a calibration when the message "high probe off-set" appears. This indicates that either the sensor is malfunctioning or the standard is contaminated.

# I.A.7: Chlorophyll

Carefully check the set screw on the chlorophyll wiper block for tightness and inspect wiper sponge for wear and color (the wiper should be white). It is recommended that the wiper be changed before all deployments. For chlorophyll, the calibration software setting should be 1 wipe (the default) every five minutes, but may need to be increased depending on fouling. For DATAFLOW a wipe should occur every fifteen minutes. The averaging interval for chlorophyll should be the default of 8. Chlorophyll calibration solutions are prepared using either an acridine orange standard solution or a rhodamine B standard solution (refer to YSI 6-Series Environmental Monitoring Systems Operations Manual). Two-point chlorophyll calibrations may not be needed at every deployment and all should only be performed in the lab. YSI recommends that the two-point calibration only be done once a month (or when drift is evident). Low end (0.0µg) calibrations are the most critical and must be done for every deployment.

#### II. DEPLOYMENT

# **II.A.**: Pre-Deployment Settings

When programming for unattended sampling, specify the site description to include information such as location, month, day, and year. The sample interval is to be set for readings to be taken every 30 minutes or less. Time convention used must be <u>Local Standard Time</u> and sampling must start on the half hour. Parameters measured must include: temperature, specific conductance, salinity, dissolved oxygen saturation, dissolved oxygen concentration, depth, pH, chlorophyll, and turbidity. It is also recommended you collect battery voltage during the deployment since these data can help identify an electrical short. After entering the program, check the battery voltage, battery life, and memory in the "set-up information" screen. If the battery life or memory is not sufficient for the length of the deployment, take appropriate action such as changing batteries or deleting files (format flash disk). The YSI 6-Series operates best with single use alkaline batteries.

# **II.B.:** Deployment Methods

All sondes will be deployed so that the probes stay submerged at low tides and are at 0.5 meters off the bottom to allow for tidal and flow amplitude measurements. The stations will be located at 1.5 meters depth MLW.

#### III. RETRIEVAL

Retrieve the sonde from the water and visually examine the probes for fouling and damage. Gently clean the sonde of debris and place it in a secure container that will prevent any severe vibrations to the unit during transportation.

# IV. POST DEPLOYMENT

# **IV.A.**: Post Deployment Calibration Check

In the laboratory a calibration check must be performed on **oxygen, conductivity, and pH probes before cleaning** and on the **turbidity probe after cleaning (to prevent contamination of the 0.0 NTU standard)**. Rinse each probe in the calibration standard (previously used is acceptable) and then compare the readings in fresh calibration standard with the instrument in discrete sample mode. Also, if previously used standards (that have **NOT** been contaminated with even DI water) are used to check calibrations, ensure these standards are never used for the primary calibrations (section I.A.). To check if the DO saturation calibration strayed, place the sonde in a calibration cup with a wet sponge, allow adequate time for the air to become saturated and temperature to stabilize (15 minutes to 2 hours depending on sonde temperature), and record the percent saturation. Post calibration checks should be done for DO %, depth, specific conductance/salinity, turbidity, chlorophyll, and pH.

### **IV.B.:** Probe Cleaning

Prior to or after the sonde is cleaned the data may be uploaded to a Personal Computer (PC) or YSI 610DM and then uploaded into a PC.

Once the post deployment calibration check is completed the sonde body and probes should be completely cleaned. Remove the sonde guard and clean all of the sensors according to the instructions in the YSI 6-Series Operations Manual. You need to pay extra attention to the instructions below.

#### IV.B.1: pH Probe

This probe should be removed from the guard to insure adequate cleaning. If fouling is not a problem, you may not need to do this for every deployment. These probes are also easily cracked so care must be taken during the cleaning process. Although cleaning with DI water is acceptable, YSI recommends cleaning this probe with tap water to ensure a full probe life.

#### IV.B.2.: DO/Cond/Temp

If significant solid material has built up near the threads of the probe, the probe should be removed from the bulkhead and cleaned. Remove the old DO membrane and inspect the probe surface. If silver electrodes show significant darkening, follow the instructions to resurface the probe face with a fine sandpaper disk found in the 6035 DO reconditioning kit. Alternatively, you can use 2400 grit sandpaper. When you change the dissolved oxygen membrane, be careful not to touch the surface of the membrane that covers the probe. Clean the conductivity sensor with the brush provided in the maintenance kit. Wet the cavities and brush, then brush both cavities several times and rinse thoroughly with water (you can also brush the cavities under

running water).

# IV.B.3.: Turbidity and Chlorophyll

Inspect the turbidity and chlorophyll wipers and replace if worn. Under normal use, the wiper will last up to 30 days of deployment time but excess fouling will shorten the life of the wiper. A dirty or disintegrating wiper is likely to cause incorrect parking of the wiper assembly during deployment. Also, a disintegrated wiper sponge may come dislodged during deployment.

#### V. YSI 6-Series DEPLOYMENT and RETRIEVAL LOG

A deployment and retrieval log must be filled out with every instrument deployment/retrieval (Appendix B). This sheet will aid in data QA/QC procedures and help identify faulty equipment. After completion, this sheet, along with the Ecowatch graph should be reviewed to identify anomalous data and faulty sondes/probes.

#### VI. VIEWING and PRINTING the ECOWatch GRAPHS

The final step in data collection is to view and print the PC6000/ECOWatch graph of all data collected during the deployment and look for patterns and outliers that can identify faulty probes and instruments. This graph must be kept with the YSI 6-Series Lab Calibration, Deployment, and Retrieval Log Sheet (tracking sheet). Both the tracking sheets and these graphs will be your best tools during the QA/QC processing of the data.

<u>CAUTION:</u> Always note the scales which are automatic by default in these programs and can mask a problem with the data set if you assume a linear scale from 0 (zero) to the probes acceptable maximum measurement.

#### VII. PROBE CARE AND STORAGE

Most of the probes, especially pH and DO, have a limited life span. The pH probes have a maximum life of 2 years (rarely longer), so any pH probes over 1 year old are near needing replacement. If probes will not accept calibrations or are slow to respond to standards, suspect aging. DO and pH probes also have a limited shelf life, so do not purchase replacements too far in advance. Dissolved oxygen probes have a life expectancy of 2-3 years.

## VII.A.: Storage

The procedure for storage is different for short-term (1 month or less) or long-term (greater than 1 month).

# VII.A.1.: Short-term Storage

For short term storage, it is important to keep the probes moist but <u>not immersed in water</u>. Keep

probes attached to the sonde and place the sonde in approx. 0.5in of water (not distilled) in the calibration cup. A moist sponge can be used in place of the 0.5in of water.

# VII.A.2.: Long-term Storage

Dissolved oxygen/conductivity/temperature and dissolved oxygen probes should be stored with membrane and electrolyte in place and place sonde in a water filled transport or calibration cup (it is important to ensure that water completely covers the DO sensor). If the probe is removed from the sonde, it should be stored with membrane and electrolyte in place and submerged in water (the conductivity cells should also be submerged). The pH probe should be removed from the sonde and stored with the pH storage cap containing 2-4 molar KCL or buffer (check manufacturers specifications). No special precautions are necessary for the chlorophyll and turbidity probes or depth/level probes.

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Appendix D: Laboratory and Sampling Protocols

# Sample Collection, Preservation, and Processing for the Continuous Surface Water Quality Mapping

# 1.0 Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS):

1.1 Water samples are collected from the effluent tubing of the DATAFLOW System in pre-rinsed (w/ambient water) darkened 1L Nalgene bottles. Exact time of collection is noted to facilitate comparison with data generated by the YSI 6600. Samples are placed in darkened bottles and packed in ice and upon return to the laboratory are processed immediately (Sections 4.0, 9.0).

# 2.0 Chlorophyll and Pheophytin:

2.1 Water samples are collected from the effluent tubing of the DATAFLOW System in pre-rinsed (w/ambient water) darkened 1L Nalgene bottles. Exact time of collection is noted to facilitate comparison with data generated by the YSI 6600. Immediately upon collection known volumes of samples are filtered through 25 mm GFF filters. Filters are folded in half and placed in plastic petri dishes covered with aluminum foil. Samples are then placed in ice and upon return to the laboratory are stored at -20°C until analyses can be conducted (Section 10.0).

# **Verification Sample Procedures for the Chesapeake Bay Nearshore Monitoring Program**

# 1.0 Total Suspended Solids and Volatile Suspended Solids

#### 1.1 Summary of Method:

- 1.1.1 A well-mixed sample of known volume is filtered through a glass-fiber filter, and the residue retained on the filter is dried to constant weight at 103 105°C.
- 1.1.2 The residue obtained from the determination of total suspended solids is ignited at 550°C for 2 hours in a muffle furnace. The remaining solids after ignition are reported as mg volatile suspended solids/L.

#### 1.2 Interferences

- 1.2.1 The principal source of error in the determination is failure to obtain a representative sample.
- 1.2.2 The test is subject to many errors due to loss of water from crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics, and decomposition of mineral salts during combustion.

# 1.3 Apparatus and Materials

- 1.3.1 47 mm glass fiber filters (GFF, 0.7 μm pore size).
- 1.3.2 Filtering Apparatus with 47mm filter holders.
- 1.3.3 Drying Oven: Capable of maintaining a temperature of 103 +2°C.
- 1.3.4 Analytical balance: Capable of weighing to 0.1 mg.
- 1.3.5 Muffle oven: Capable of heating to  $550^{\circ}$ C.

# 1.4 Sample Handling

1.4.1 Preservation of the unfiltered sample is not practical; analysis should begin as soon as possible. Refrigeration or icing minimizes the microbiological decomposition. After filtering, the filter can be stored frozen at -20 °C for 28 days.

#### 1.5 Procedure:

- 1.5.1 Preparation of filters for Total Suspended Solids (TSS) and Volatile Suspended Solids (VSS):
  - 1.5.1.1 Pre-number aluminum weigh boats (i.e. 1,2, etc.).
  - 1.5.1.2 Place filters wrinkled side up on clean filtering apparatus.
  - 1.5.1.3 Run three successive 30 mL washes of ASTM Type I water through each filter while applying suction. Do not exceed a vacuum of 10 psi.
  - 1.5.1.4 Allow suction pump to run until the filters are "dry".
  - 1.5.1.5 Carefully transfer filters to pre-numbered weigh boats using forceps.
  - 1.5.1.6 Ignite blank filters in the muffle furnace at 550°C for approximately 15 to 20 minutes.
  - 1.5.1.7 Place filters in a desiccator until cool.
  - 1.5.1.8 After cooling (approximately 15 minutes), weigh filters on an analytical balance capable of measuring to 0.1 mg. Record weights and return filters to weigh boats.
  - 1.5.1.9 Return filters to the oven for at least 1 hour. Reweigh filters a second time. Filter weights must not be more than  $\pm$  0.5 mg. If greater, return filters to oven for at least 1 more hour.
  - 1.5.1.10 After dry weights have been determined, filters are stored in their aluminum weigh boats in an airtight container until needed.
- 1.5.2 Determination of Suspended Solids:
  - 1.5.2.1 Place pre-weighed filter on a clean filter holder with wrinkled side up. Turn on vacuum pump. Do not exceed a vacuum of 10 psi.
  - 1.5.2.2 <u>Vigorously</u> shake sample.
  - 1.5.2.3 Rinse 250 mL graduated cylinder with a small quantity of sample.

- 1.5.2.4 Measure 250 mL of sample into cylinder and pour into the filtering funnel. Repeat for a total volume of 500 mL. Smaller volumes may be used if sample has a great deal of suspended matter or larger volumes may be used if sample has low levels of suspended matter.
- 1.5.2.5 Record volume filtered (mL).
- 1.5.2.6 Rinse filter with DDI water to remove salts.
- 1.5.2.7 Allow the vacuum pump to run until filter is "dry".
- 1.5.2.8 Run one duplicate (500 mL sample, 500 mL duplicate) for every set of ten samples. If less than ten samples are run, then one duplicate should be made.
- 1.5.2.9 Remove filter with forceps.
- 1.5.2.10 Place filter in numbered weigh boat. Dry to a constant weight in a 103-105°C oven at least 4 hours (preferably overnight).
- 1.5.2.11 Place filters in desiccator until cool.
- 1.5.2.12 Repeat weighing procedure
- 1.5.2.13 Return filters to the oven for at least one hour.
- 1.5.2.14 Repeat weighing procedure. If filters do not weigh within ±0.5mg of their first weight, the process of drying and weighing should be repeated as many times as needed to achieve this constant weight.
- 1.5.2.15 For VSS muffle filters for 15 minutes at 550°C. Repeat weighing procedure.
- 1.6 Calculation

mg volatile suspended solids/L =  $(A-B) \times 1000$ sample volume, mL

mg total suspended solids/L =  $\frac{\text{(A-C)} \times 1000}{\text{sample volume, mL}}$ 

where:

A = weight of residue + filter before ignition, mg

B = weight of residue + filter after ignition, mg

C = weight of filter, mg

# 1.7 Reference(s):

U. S. EPA. 1979. <u>Methods for Chemical Analysis of Water and Wastes</u>, Method 160.2.

Standard Methods, 18<sup>th</sup> edition, pp. 2-54 to 2-57.

### 2. Chlorophyll and Pheophytin

# 2.1 Scope and Application:

2.1.1 Chlorophyll data may be used to determine long-term trends in water quality and the trophic status of surface waters, to detect adverse effects of pollutants on plankton, and to provide estimates of studies attempting to estimate algal biomass and productivity.

# 2.2 Summary of Methods:

2.2.1 The method for determining Chlorophyll *a* given here is with a Turner Design fluorometer. The method used requires filtering a known quantity of water through a glass fiber filter. This filter is later ground with a tissue grinder made of teflon/glass. Approximately 1-3mLs of 90% acetone are added to the filter before grinding. Acetone is also used to wash the filter into 17 x 150 test tube with tight fitting cap. The sample is steeped at least 2 hours and not exceeding 24 hours at 4°C, in the dark. The samples are centrifuged and read on a fluorometer. If the samples can not be read within that time period, storage in the freezer at -20°C for a few days is acceptable. If pheophytin measurements are desired, the sample is acidified and read again.

# 2.3 Reagents:

NOTE: Use fresh, distilled, DDI water. Label, date, and initial all reagents.

2.3.1 Aqueous Acetone solution (90%) - Mix 90 parts acetone (Optima grade) with 10 parts DDI water. Add 4 drops of 1N NaOH/L.

Note: Mix the reagents in the appropriately marked bottle in the following order: 1800 mL Acetone, 200 mL DDI water, 8 drops 1N NaOH. This is to be stored in the yellow FLAMMABLE cabinet.

#### 2.4 Equipment:

2.4.1 The Turner Designs TD-700 Laboratory Fluorometer is now used in this laboratory to make chlorophyll A and pheophytin determinations. The Fluorometer is equipped as follows:

## 2.4.1.1 Daylight White Lamp P/N 10-045

2.4.1.2 Filters (For Chlorophyll A and Pheophytin measurements)

Excitation: 340-500 nm P/N 10-050R Emission: >665 nm P/N 10-015R

Filters (For Chlorophyll A only) P/N 10-113

Emission: 680 nm P/N 10-115

- 2.4.2 Centrifuge capable of holding the 17 x 150mm tubes.
- 2.4.3 Tissue grinder and equipment Teflon/glass type pestles, electric motor, stand and glass grinding vessels.
- 2.4.4 Centrifuge culture tubes 17x 150 mm culture tubes with tight fitting caps.
- 2.4.5 Filtration equipment Vacuum pump (vacuum should not exceed 1/2 atm or 15psi, filter holder for 47mm GF/F filters, 47mm GF/F filters, 2X4 ziplock bags, foil or a dark storage container.

# 2.5 Standards

- 2.5.1 Fluorometer BLANK: (Used as a "Filter Blank"). An unfiltered blank filter will be analyzed as if it were a sample, extracted as described in Volume V, Section 5.
- 2.5.2 Calibration Standard: Standards are obtained from Turner Instruments. Calibration standards consist of a minimum of one high standard and one low standard maintained in 90% acetone. An intermediate standard may be made by diluting the high standard appropriately with 90% acetone. This solution should be determined to be a high purity blank. Calibration Standards should be frozen at -20 °C prior to use.

#### 2.6 Calibration of Fluorometer

2.6.1 Calibration Standards and a Calibration Blank (90% optima grade acetone) are required for this step

- 2.6.2 Proceed to Calibration set-up menu on the TD-700 fluorometer. A minimum of two standards should be used for the calibration. Three standards and a blank are optimal.
- 2.6.3 Use A multi-optional@ mode with / Direct Concentration/ug/L units
- 2.6.4 Calibration
  - 2.6.4.1 Enter Highest Standard first. Key in the high concentration value. Insert test tube with high standard in fluorometer. Press <\*> when stable. The sensitivity setting will be automatically set. The fluorometer will read the high standard then ask for subsequent standards.
  - 2.6.4.2 When all standards have been read, insert the blank.
  - 2.6.4.3 Press <0> when the value is stable.
  - 2.6.4.4 Calibration will be completed
- 2.6.5 Acid Ratio Determination:
  - 2.6.5.1 The acid ratio (the ratio of the fluorescence of any extract containing only chlorophyll, before and after the addition of acid) should be determined for each fluorometer run.
  - 2.6.5.2 Calibrate the fluorometer as described in Section 5.5.
  - 2.6.5.3 Reread intermediate calibration standard (R<sub>b</sub>)
  - 2.6.5.4 Acidify the standard with 2 drops of 0.1N HCL. Mix. Wait 90 seconds.
  - 2.6.5.5 Read sample as  $R_a$ .
  - 2.6.5.6 Acid ratio

 $R = R_b/R_a$ 

- 2.7 Procedure:
  - 2.7.1 Grinding procedure

NOTE: Before grinding set up samples by listing the sample ID and volume on the bench sheets. Label small pieces of white tape with the ID volume, apply these to the culture tubes.

- 2.7.1.1 Close half-curtain around grinding area. This blocks out fluorescent light which destroys chlorophyll. Turn on the incandescent light and the hood fan.
- 2.7.1.2 Place filter in grinding vessel and add 1-3mL of the 90% acetone.
- 2.7.1.3 Insert pestle in grinding tube, and turn on grinder by using switch on post of apparatus. NEVER turn on the grinding motor without having the pestle in the vessel.
- 2.7.1.4 Thoroughly grind filter for approximately 2 minutes. Be sure there are no discernable pieces left. Pull pestle to the top of the vessel and rinse lightly with the 90% acetone.
- 2.7.15 Rinse pestle with 20 ml of 90% acetone into the culture tube.
- 2.7.1.6 Cap tube and shake lightly.
- 2.7.1.7 Store tubes in racks in a closed box and place in refrigerator for 2-24 hours. The sample tubes may be stored for a couple of days at -20°C if necessary.

#### 2.7.2 Centrifuging samples

- 2.7.2.1 Before removing samples from closed box, turn off lights. Fluorescent light destroys chlorophyll!
- 2.7.2.2 Shake samples to ensure thorough mixing.
- 2.7.2.3 Place samples in centrifuge in an order that can be remembered (tubes must be kept in order).
- 2.7.2.4 Close cover until it clicks. Adjust setting to approximate 675g.
- 2.7.2.5 Turn TIME/MIN knob to 15 minutes. This starts the centrifuge spinning.

- 2.7.2.6 After centrifuge has stopped spinning, open top (pull up firmly on lever on top of cover), remove tubes and replace in rack. Check the order against sheets.
- 2.7.3 Reading on Fluorometer
  - 2.7.3.1 Pipette samples into fluorometric cuvettes.
  - 2.7.3.2 Read sample in fluorometer. Results are read in direct concentration.
  - 2.7.3.3 Read sample; record as R<sub>B</sub>.
  - 2.7.3.4 Add 2 drops of 0.1 N HCL and shake well.
  - 2.7.3.5 Read sample record as R<sub>a</sub>.
- 2.8 Calculations:
  - 2.8.1 For uncorrected Chlorophyll A using Method 445.0 with acidification: (Instrument must be equipped with Excitation: 340-500 nm P/N 10-050R Emission: >665 nm P/N 10-015R)
    - $2.8.1.1 C_{E,u} = R_b \times F_s$

Where:  $C_{E,u}$  = uncorrected chlorophyll A concentration (ug/L) in the extract solution analyzed

R<sub>b</sub> = fluoresence response of sample extract before acidification, and

F<sub>s</sub> = fluorescence response factor for sensitivity setting S (which =1 for the TD-700 fluorometer)

2.8.1.2 Calculate the "uncorrected" concentration of chlorophyll A in the whole water sample as follows:

 $C_{S,u} = C_{E,u} \times extract \ volume \ (L) \times DF$ Sample volume (L)

Where:  $C_{S,u}$  = uncorrected chlorophyll A concentration (ug/L) in 6the whole water sample

Extract volume = volume (L) of 90% acetone used for extraction of the filter

DF = Dilution factor

Sample volume = volume (L) of whole water filtered through filter

2.8.2 For corrected Chlorophyll A using Method 445.0 with acidification:

2.8.2.1 
$$C_{E,C} = F_s (r/r-1) (R_b - R_a)$$

Where:  $C_{E,C}$  = corrected chlorophyll A concentration (ug/L) in the extract solution analyzed

 $F_s$  = response factor for sensitivity setting S,

r = the before to after acidification ratio of the pure chlorophyll standard

 $R_b$  = fluorescence of sample extract before acidification, and

 $R_a$  = fluorescence of sample extract after acidification

2.8.2.2 Calculate the @corrected@ concentration of chlorophyll A in the whole water sample as follows:

$$C_{S,C} = C_{E,U} \times extract \ volume \ (L) \times DF$$
  
Sample volume \((L)\)

Where:  $C_{S,C} = corrected \quad chlorophyll \quad A \quad concentration \ (ug/L) \ in the whole water sample$ 

Extract volume = volume (L) of 90% acetone used for extraction of the filter

DF = Dilution factor

Sample volume = volume (L) of whole water filtered through filter

2.8.2.3 For corrected pheophytin using Method 445.0 with acidification:

$$P_{E} = F_{s} (r/r-1) (rR_{b}-R_{a})$$

## $P_S = \underline{P_E} \underline{x} \underline{extract \ volume (L) \ x \ DF}$ Sample volume (L)

Where:  $P_E$  = pheophytin concentration (ug/L) in the sample extract, and

P<sub>S</sub> = pheophytin concentration (ug/L) in the whole water sample

- 2.8.3 For Corrected Chlorophyll A using Method 445.0 without acidification: (Instrument must be equipped with Excitation: 436 nm P/N 10-113 Emission: 680 nm P/N 10-115)
  - 2.8.3.1 Calculate the correct concentration of chlorophyll A in the whole water sample as follows:

$$C = \underline{C_C \times \text{extract volume (L)} \times \text{DF}}$$
Sample volume (L)

Where: C = corrected chlorophyll A concentration (ug/L) in the whole water sample

C<sub>C</sub> = corrected chlorophyll A concentration (ug/L) in the extract solution analyzed

Extract volume = volume (L) of 90% acetone used for extraction of the filter

DF = Dilution factor

Sample volume = volume (L) of whole water filtered through filter

## 2.9 Reference(s):

Strickland, J.D.H., and Parson, T.R. 1972. <u>A Practical Handbook of Seawater Analysis</u>. Fish. Res. Bd. Canada 167:310.

<u>TD-700 Laboratory Fluorometer Operating Manual.</u> Version 1.8. July 7, 1999. Turner Designs, 845 West Maude Avenue, Sunnyvale, CA 94086.

EPA /600/ R-97/072 - Method 445.0. *In Vitro* Determination of Chlorophyll a and Pheophytin a in Marine and Freshwater Algae by Fluorescence. Methods for the Determination of Chemical Substances in Marine and Estuarine Environmental Matrices Revision 1.2. September 1997.

<u>Using the Turner Designs Model 10 Analog, The 10AU Digital, Or the TD-700 Fluorometer with EPA Method 445.0</u>. January 19, 1999. Turner Designs, 845 West Maude Avenue, Sunnyvale, CA 94086

#### 4.0 Secchi Depth

#### 4.1 Scope and Application

4.1.1 The turbidity of natural water is a critical factor in sustaining submerged aquatic vegetation as well as epiphyte and phytoplankton growth.

## 4.2 Summary of Method

4.2.1 A black and white secchi disk that is attached to a weighted, ruled line is lowered slowly into the water until it disappears and then raised. The depth at which the disk disappears is averaged with the depth at which it reappears; this measurement (in meters) is the secchi depth.

#### 4.3 Procedure

- 4.3.1 A round, weighted secchi disk measuring 20cm in diameter is used. The upper surface is divided into four equal quadrants that are colored so that the two quadrants opposite each other are black and the intervening ones are white. It is attached to a ruler line that is marked in 0.1m intervals.
- 4.3.2 Readings with the secchi disk are made in situ without the aid of sunglasses on the shady side of the vessel to reduce possible sun glint on the water surface.
- 4.3.3 The disk is slowly lowered into the water until it disappears and then raised. The depth at which the disk disappears is averaged with the depth at which it reappears; this measurement (rounded to the nearest 0.1m increment) is the secchi depth.
- 4.3.4 The secchi disk is not permitted to touch the sediment surface. If the secchi depth exceeds the water depth in shallow water no measurement is recorded and the profile is repositioned in slightly deeper water.
- 4.3.5 The time of the secchi measurement is recorded. For continuous surface water quality verification stations and fixed stations this facilitates matching of secchi depth readings with transmissometer (NTU) data.

## 4.4 Quality Control

- 4.4.1 Reported Units 4.4.1.1 (0.1m)
- 4.5.1 Detection Limits 4.5.1.1 Upper Limit - N/A 4.5.1.2 Lower Limit - 0.1m

## 4.5 References

Tyler, John. 1968. The secchi disk. Limnol. Oceanogr. 13 (1): 1-6.

# 5.0 <u>Attenuation of Underwater Photosynthetically Available Radiation (PAR 400-700nm)</u>

### 5.1 Scope and Application

5.1.1 Light attenuation of PAR through the water column is an important apparent optical property of natural water that is a critical factor in sustaining SAV and well as regulating epiphyte and phytoplankton growth. The degree of this attenuation is related largely to the concentration of suspended and dissolved substances in the water. PAR is that component of the solar radiation spectrum that is typically defined as visible light and within this range of wavelengths are those predominantly used by plants for photosynthesis.

### 5.2 Summary of Method

- 5.2.1 Downwelling light penetrating the water column (PAR) is measured underwater at several depths to calculate the light attenuation coefficient, Kd. This procedure may also be used to estimate the depth of the photic zone. Concurrent incident light readings are taken on deck with each depth measurement. Simultaneous deck and submersed measurement are necessary because of variability in incident surface irradiance due to changing atmospheric conditions (i.e. cloud cover).
- 5.2.2 Kd is calculated as the negative exponential decay function of underwater light with depth. Light is typically measured as the quantum flux of downwelling irradiance using cosine-corrected downwelling quantum sensors.
- 5.2.3 Equipment: manufactured by LI-COR, Inc.
  - 5.2.3.1 LI-192SA, Underwater Quantum Sensor
  - 5.2.3.2 LI-190SA, Quantum Sensor (deck)
  - 5.2.3.3 Li-1000 or LI-1400 Datalogger

#### 5.3 Procedure

5.3.1 PAR is determined from the sunny side of a vessel or pier during daylight hours. Both deck and submersed sensors must be away from the shadow of the vessel or objects on the vessel.

- 5.3.2 Check the sensor operation by connecting the deck sensor and underwater sensor to corresponding ports of the Li-Cor data logger, and turn the power on. Check battery level. Cover each sensor and check to see if the output is very near zero. Place the sensor under a light source to assure that it has a positive reading. A negative reading indicates that the polarity of the sensor is reversed (it is plugged into the cable backwards). A very positive or negative reading under dark indicates a possible short in the cable or some other electrical short.
- 5.3.3 In the field, mount the deck sensor in a location that is level and unobstructed by shadows. Ensure that sensors are positioned properly on the deck sensor mounting and the lowering frame. Connect deck sensor and underwater sensor to corresponding ports of the meter, and turn the power on.
- 5.3.4 Set instrument averaging constant to display results from previous 10 or 15 seconds.
- 5.3.5 Lower the frame until the sensor is just below the surface of the water. At a depth of 0.1 meter (~ 4 inches), simultaneously record the deck sensor and the underwater readings. If wave action prevents this, take the initial reading at 0.5 meters. Depth of the underwater sensor diffuser below the surface of the water is determined with a calibrated pole or non-stretching rope.
- 5.3.6 Lower the frame and take subsequent measurements at depths appropriate to the monitoring location and purpose of the project (see below). Allow the instrument output to stabilize, at least for the averaging period, then record both deck and underwater readings at each depth.
- 5.3.7 The simultaneous deck and submersed readings are stored by pressing "Enter". Each record will be stored with a time stamp which will flash on the data logger readout. Record this time. All readings can be subsequently retrieved at the end of the cruise.
- 5.3.8 Mainstem and Tidal Tributary Photic Zone. Record initial PAR at a depth of 0.1 meter below the surface. At mainstem stations, record subsequent measurements at 1 meter intervals, and in the tributary stations, at 0.5 meter intervals when total depth is greater than 2 meters. If depth to bottom is less than 2 meters, take readings at 0.25 meter increments.

- 5.3.9 Measurements are recorded until the meter reads <1% of the initial subsurface value, or if the bottom is reached. If water is clear and deep, the increments may be increased to 2 meters. If water is turbid or colored, (low secchi depth), 0.25 meter increments may be appropriate.
- 5.3.10 <u>Data Flow Mapping and High Frequency Meter Regressions</u> Record initial PAR at a depth of 0.1 meter below the surface. When depth to bottom is less than 2 meters, record 3 to 4 additional PAR measurements at 0.25, 0.5, 0.75 and 1.0 meters. When depth to bottom exceeds 2 meters, record PAR at 5 depths (e.g., 0.1, 0.5, 1.0, 1.5 and 2.0 meters).
- 5.3.11 Replicate PAR profile at each location to make sure readings are correct.

#### 5.4 Quality Control

- 5.4.1 The deck cell should have the highest PAR value, and the underwater sensor output should decrease as the sensor is lowered.
- 5.4.2 Periodically check that sensors are linear and not out of calibration with respect to each other.
- 5.4.3 Calibration of the sensors by LICOR, Inc. is recommended every year, and required every two years.(AMQAW, 2002)

#### 5.5 Kd Calculations

- Light measurements are taken simultaneously of both surface ( $I_0$ ) and submarine PAR intensity ( $I_{z+n}$ ). Submarine PAR is measured at the surface (0.1 meters), and successive intervals thereafter ( $I_{z+1}$ ,  $I_{z+2}$ ,...  $I_{z+n}$ ).
- 5.5.2 Each deck reading is normalized to an arbitrary deck reading of  $2000 \, \Box$  mol m<sup>-2</sup> sec<sup>-1</sup> and the simultaneously recorded submarine reading is multiplied by this ratio to correct the individual submersed readings of each profile for any difference in solar insolation intensity during the profile. The attenuation coefficient  $(K_d)$  can then be calculated between any two depths on one profile as:

$$K_{z,z+n} = \ln(I_{z+n}/I_{z+(n-1)})$$

$$\Delta z$$

where:

 $K_{z,z+n}$  = attenuation coefficient (m<sup>-1</sup>) over the depth interval z+n,z+(n-1)  $I_{z+n}$  = normalized PAR intensity at depth z+n (µmol m<sup>-2</sup>s<sup>-1</sup>), (i.e, deeper value)

 $I_{z+(n-1)} = \text{normalized PAR intensity } z+(n-1) \text{ depth } (\mu \text{mol m}^{-2}\text{s}^{-1})$ 

 $\Delta z = \text{difference in depth (m) between } z+n, z+(n-1)$ 

5.5.3 For more than two depths on one profile plot the natural log of each normalized PAR value on the x-axis vs. depth. The slope of the line times (-1.0) is Kd.

## 5.6 Reporting

- 5.6.1 The CIMS data base stores PAR values from the deck sensor and each underwater measurement under the following method codes:
  - 5.6.1.1 EPAR D F01: Flat Cosine Quantum Sensor LI-192SA
  - 5.6.1.2 EPAR\_S F01: Deck (reference) Quantum Sensor LI-190SA
  - 5.6.1.3 SDEPTH: Sample depth at which PAR reading is recorded, in meters

### 5.7 References

Kirk, J.T.O. 1994. <u>Light and photosynthesis in aquatic ecosystems</u>. 2<sup>nd</sup> ed. University Press, Cambridge. 509 pp.

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Appendix E: DATAFLOW QA/QC Protocol

- 1. Data Processing for EPA Dataflow Project
- 2. For each tributary a folder is created with the year (ex York River 2004)
  - 2.1. In this folder each cruise date gets a folder (ex Apr 23)
  - 2.2. In this folder are a series of files
    - 2.2.1. The raw text file (ex 230802.txt)
    - 2.2.2. The raw excel file (ex RawYRKPH04-23-04)
    - 2.2.3. The first cut QAQC File (ex YRKPH04-23-04)
    - 2.2.4. A file w/ station averages graphs (ex YRKPH04-23-04Averages Graphs)
    - 2.2.5. A GIS file with all bad data coded -999 (ex GISYRKPH04-23-04)
    - 2.2.6. A file with the EPA format and error codes (ex YRKPH04-23-04EPA)
    - 2.2.7. There is also a Tributary Metadata File (ex York 2004 Metadata)
      - 2.2.7.1. YSI Post Cal for all parameters
      - 2.2.7.2. Date and Location of cruise
      - 2.2.7.3. Time stamp of all deleted data due to electronic interference
      - 2.2.7.4. Time stamp of data line with no depth information
      - 2.2.7.5. Time stamp with any questionable data and action taken
      - 2.2.7.6. Track the process of QA-ing the file (see example Metadata file)
- 3. Download data from field computer
  - 3.1. Original file is left on field computer
  - 3.2. Data file is backed up in "Raw Downloads" folder
    - 3.2.1. Data is also placed into the Tributary file under Date of cruise (see above formatting)
- 4. The macro (ex. moore df EPA) is opened in Excel
  - 4.1. The raw text file is opened in Notepad
  - 4.2. Entire file is selected and pasted into Excel
  - 4.3. Macro is run on the raw file (text to columns, headers, convert lat lon to correct form, etc)
  - 4.4. The file is then saved as RawCBPSegmentmm-dd-yy.xls (ex RawYRKPH04-23-04.xls)
- 5. First round of QAQC
  - 5.1. Save file as *CBP segmentmm-dd-yy*.xls (remove *Raw*)
  - 5.2. Delete all data up to the recorded cruise track start time, record in metadata
  - 5.3.Delete the following fields
    - 5.3.1. **GPS** Time
    - 5.3.2. GPS Quality
    - 5.3.3. Lat Dir
    - 5.3.4. Lon Dir
    - 5.3.5. Heading
    - 5.3.6. Date
    - 5.3.7. Unknown

- 5.4. Delete all incomplete data caused by electronic interference, record in metadata
- 5.5. Look for gaps in data due to running aground, pulling intake, GPS malfunction, computer malfunction, and depth sounder malfunction
- 5.6. Replace all \*57 depth errors with -999 and record in metadata
- 5.7. Examine all field notes noting events such as running aground, blooms, etc
  - 5.7.1. Examine the data for effects of these events
  - 5.7.2. Highlight any questionable data and note in metadata with time stamp
  - 5.7.3. If an event did not affect the data note this also
  - 5.7.4. Save file as *CBPSegmm-dd-yy*.xls (ex. YRKPH04-23-04.xls)
- 6. YSI Post Calibration information
  - 6.1 Looking at the post cal notes see that all parameters post cal within limits
    - 6.1.1. Acceptable limits listed in table below
  - 6.2.Enter all info into the metadata for that cruise date
  - 6.3. Highlight any data that falls outside the limits and record in metadata
  - 6.4. If made any changes to CBPSegmm-dd-yy.xls resave
- 7. Second Round QAQC Station Averages
  - 7.1.Resave the step 5 file as CBPSegmm-dd-yyAverages Graphs.xls
  - 7.2.Locate the time stamp of each station on the field data sheets
  - 7.3. Highlight the data string line
    - 7.3.1. Record Lat and Lon on the field data sheet in appropriate location
    - 7.3.2. In the excel sheet find the Average of the 10 observations before and after the station (If the optical sensors wipe during this time...use 10 obs before or after the wipe). Record on field data sheet in appropriate place
- 8. Second Round QAQC Graphs
  - 8.1. Using the Scatter with data points connected by lines Chart Type in Excel
  - 8.2. Graph Wtemp, Salinity, DO mg/l, pH, Turb, and Chl over time
  - 8.3. Examine each graph carefully for any "strange" data
    - 8.3.1. Unexplained plumes in data

Look at the surrounding data and the depth. If there is no indication of probe failure or stirring up the bottom, leave data in the data set, a comment if it is questionable can always be added to the comments column later

- 8.3.2. Single spikes or drops in values

  To determine if a single spike should be flagged, take the Standard

  Deviation of the 10 numbers before and after the questionable value.
  - Deviation of the 10 numbers before and after the questionable value and if the value is <> 3 times the Stdev highlight it
- 8.3.3. Negative CHL and NTU data
- 8.3.4. Strange patterns in DO data
- 8.3.5. Any indications of probe issues
- 8.3.6. Record any abnormalities on metadata and highlight in spreadsheet
- 9. Second Round QAQC Visual Check

- 9.1. Using the same file take a closer look at patterns of data
- 9.2.Record any issues on metadata with time stamp and highlight in spreadsheet
  - 9.2.1. Examine DO data
  - 9.2.2. Examine CHL data
  - 9.2.3. Examine NTU data
  - 9.2.4. Remember to use verification data to verify highs in data

## 10. Final QAQC

- 10.1. Using all the appropriate information decide what data is "bad" and assign error code (record in metadata)
- 10.2. If data is questionable but there is not a reason to actually mask it with error put information into COMMENT column (record in metadata)
- 11. Rectifying Files (CBPSegmm-dd-yy.xls and CBPSegmm-dd-yyAverages\_Graphs.xls)
  - 11.1. Using the metadata records with time stamps go back to original file
  - 11.2. Highlight all data which has been determined to be questionable
  - 11.3. On the Aver\_Graphs file clear content of all questionable cells
  - 11.4. Reexamine parameter graphs to look for any other anomalies
  - 11.5. Note all actions and progress in metadata
  - 11.6. When two files are exactly the same note in metadata

#### 12. Create GIS File

- 12.2. Open original file and resave as GISCBPSegmm-dd-yy.xls
- 12.3. Replace any questionable data with -999
- 12.4. Remove all highlights, colors etc in the data
- 12.5. Save and record in metadata
- 12.6. Record when GIS file was passed on to GIS Tech

#### 13. Create EPA file

- 13.2. Open Excel and DFtoEPAFormat macro
  - 13.2.1. Open original file CBPSegmm-dd-yy.xls
  - 13.2.2. Select the whole file and copy and past it into the macro sheet
  - 13.2.3. Add a column after the CHL column
  - 13.2.4. Run the DFtoEPAFormet macro
  - 13.2.5. Save as *CBPSegmm-dd-vy*EPA.xls
- 13.3. Add in information in the following columns
  - 13.3.1. PROJECT = DFLO
  - 13.3.2. SOURCE = VIMS or HRSD
  - 13.3.3. STATION = PRI SEG (Primary Segment covered by cruise)
  - 13.3.4. CRUISE TRACK = xxxmmddyyyy (xxx 3 letter Trib code)
  - 13.3.5. WATER\_BODY = River Name (YORK RIVER)
  - 13.3.6. PRI SEG = Primary Segment covered by cruise
  - 13.3.7. SONDE = the serial number of YSI used
  - 13.3.8. DEPTH = 0.50

### 13.3.9. LAYER = BS

- 13.3.10. Then fill in the appropriate unit and method for each parameter (see chart below for that information)
- 13.4. Using the metadata and highlights add the appropriate error codes (see attached list of error codes and meanings as well as comments)
- 13.5. Remove all highlights and colors and save the file
- 13.6. If there are still questions about the file note in metadata

## Acceptable Limits of YSI Post Calibration

Parameter	Value
Chlorophyll	±5 % of true value
Dissolved Oxygen	±0.5 mg/L
PH	±0.2 pH units
Specific Conductance	±5 % of true value
Turbidity	±5 % of true value
Water Temperature	±0.2 °C

### Parameter Units

<u>Parameter</u>	<u>Units</u>	Method Code
TOTAL_DEPTH	M	-
BATT	-	-
BOAT_SPEED	KNOTS	-
WTEMP	DEG C	F01
SPCOND	UMHOS/CM	F01
SALINITY	PPT	F01
DO_SAT	PCT	F01
DO	MG/L	F01
PH	SU	F01
TURB_NTU	NTU	F01 for 6136 or F02 for 6026
FLUOR	%FS	NA
TCHL_PRE_CAL	UG/L	F01
CHLA	UG/L	NND

## DATAFLOW & Continuous Monitoring Specific Error Codes

<u>Category</u>	<u>Code</u>	<b>Description</b>
Specific Probe Code	$\overline{ extsf{PSW}}$	Salinity Calibrated to Incorrect Level
Specific Probe Code	PDP	DO Poisoning (anoxia)
General Probe Code	GBO	Blocked Optic

General Probe Code	GWM	Wiper Malfunction
General Probe Code	GWL	Wiper Lost
General Probe Code	GSC	Seal Compromise
General Probe Code	GPF	Probe Failure
General Probe Code	GPC	Post Calibration Out of Range
General Probe Code	GNV	Negative Value
Non-Probe Codes	NPF	Power Failure
Non-Probe Codes	NOW	Instrument Out of Water
Non-Probe Codes	NNF	Ram Clogged/No Flow
Non-Probe Codes	NND	No Data
Non-Probe Codes	NIS	Invalid Data Due to Incorrect YSI Setup
Non-Probe Codes	NIR	Instrument Removed
Non-Probe Codes	NQR	Data Rejected Due to QA
Comments	CTS	Time Skip
Comments	CBF	Biofouling
Comments	CWD	Instrument at Wrong Depth
Comments	CTF	Temperature Probe Failure
Comments	CSW	Salinity Level Calibrated Incorrectly
Comments	CLF	Flow Low
Comments	CDB	Disturbed Bottom
Comments	CTC	Time Change
Comments	CTW	Turbid Water
Comments	CFK	Fish Kill
Comments	CSC	Site Location Change
Comments	CAS	Algal Sample Taken
Comments	CAB	Algal Bloom – No Sample Taken

See  $\underline{\text{http://www.chesapeakebay.net/pubs/cbwqdb2004}\_\text{RB.PDF}}$  for any questions parameter units, other error codes, method codes, etc

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Appendix F: DATAFLOW GIS Protocol for Interpolations & Cruise Tracks

## Water Clarity Acres Determination Methodology

- 1. Create analysis grids
  - a. Create segment analysis grid (analysis\yp).
    - i. The Chesapeake Bay segments, (James tidal fresh split, 92 segments) coverage is used for the polygon input (baselayers\cbsegsplit -cov).
    - ii. Import coverage into blank ArcMap document.
    - iii. Select target segment
    - iv. Right click the layer and select Data → Export Data
    - v. Save the file as baselayers\yp.shp and add the newly created file to the map
    - vi. Open Feature to Raster Tool
      - 1. Input features = features created in 1av.
      - 2. Output Raster = baselyrs\yp\_tmp
      - 3. Field = cbpseg
      - 4. Set extent to include at least entire available bottom (bathymetry = 0-2m) for the segment.
      - 5. Round extent to nearest 25 meters (for yrkph segment, we use top: 4138875, left: 352575, right: 376775, bottom: 4117725).
      - 6. Cell Size = 25m.
      - 7. Projection = NAD 1983 UTM Zone 18N.
    - vii. Open Multi Output Map Algebra tool
      - 1. expression: segmask = con(isnull(setnull(cbseg\_tmp = = 0,cbseg\_tmp)).0.1)
      - 2. where, segmask = analysis grids\yp
      - 3. cbseg tmp = analysis grids\yp tmp
    - viii. Delete analysis grids\yp tmp in ArcCatalog
  - b. Use Feature to Raster Tool to create bathymetry grid (analysis\ypbathy).
    - i. Use .5 meter Chesapeake Bay bathymetry (baselayers\bathy0502 cov)
    - ii. Field = Tier
    - iii. Use same extent and cell size as in step 1a.
  - c. Use Feature to Raster Tool to create current SAV grid ("analysis\yp 06").
    - i. Use VIMS SAV coverage for most current year ("baselayers\beds06" cov)
    - ii. Field = Density
    - iii. Use same extent and cell size as in step 1a.
  - d. Use Feature to Raster Tool to create exclusion zone grid ("analysis\ypxz").
    - i. Use Chesapeake Bay no grow zones ("baselayers\nogrow zones" cov)
    - ii. Field = Exclude
    - iii. Use same extent and cell size as in step 1a.
- 2. Query VECOS database
  - a. Query dataflow data for single date and segment from VECOS. Note: The query is designed to take each unique combination of SAMPLE DATETIME

- (combination of date and time for each point sampled by dataflow), LATITUDE, & LONGITUDE. This is done because sometimes there is duplicate data for the same time or same location. In these instances, the query is designed to take the mean for each duplicate measurement of SALINITY, CHLA, AND TURBIDITY. The query also assigns a value of -999 where data has an associated error code.
- b. Save the result of the query as a table in an access database (db = "wq\_data.mdb", table = "yp052907"). Note: Example table has more parameters than salinity, chla, and turbidity. However, they are not necessary for this analysis. In table: salinity = sa\_mean, chla = ch\_mean, and turbidity = tu\_mean.
- 3. Copy table into ArcGIS geodatabase (gdb = wq\_data.gdb, table = yp052907).
- 4. Create point feature from table
  - a. Open New ArcMap document. Add table (wq\_data.gdb \yp052907)
  - b. Right click on table and select "Display XY Data"
    - i. X field = Longitude
    - ii. Y field = Latitude
    - iii. Projection = GCS North American Datum 1983
  - c. Use Project tool to project XY event layer
    - i. Input = event layer
    - ii. Projection = NAD 1983 UTM Zone 18N
    - iii. Output = geodatabase (gdb = wq data.gdb, table = "yp052907p")
- 5. Check for any outlying spatial points (rarely, Lat/Long is wrong in the table as in the example). Delete any outlying points from dataset in an ArcMap edit session. Save edits. May need to repeat step 4c on edited feature if zoom-layer does not focus on remaining points. Output: gdb = wq data.gdb, table = "yp052907p")
- 6. Add resulting point feature to blank ArcMap document
- 7. Select where ch\_mean > -999. Note how much data may be invalid. Decide if too much data has an associated error code to proceed with interpolation for this dataset. This decision is made with a concern for the amount and spatial distribution of data that will be excluded. In the future, we would like to move toward a less-subjective approach though the use of an associated standard error grid. If the interpolation is not made, that particular date is ultimately thrown out of any annual mean water clarity acreage calculations. If there is sufficient data to continue, clear the selection before continuing with the interpolation.
- 8. Create the Ordinary Kriging Prediction Map (\*\*For segments where interpolations will be executed without the use of barriers. For segments where barriers are used (currently rpptf, rppoh, and all Potomac creeks), see alternative steps 8 and 9 at the end of this document).
  - a. From the Geostatistical Analyst toolbar, choose Geostatistical Wizard

- b. In the Choose Input Data and Method dialog box
  - i. Input Data: current feature (should default to the correct file)
  - ii. Attribute: choose the parameter for interpolation (ch mean).
  - iii. Check the Use NODATA value: box and enter -999 as the NODATA value
  - iv. Choose Kriging in the Methods box (or allow to default)
  - v. Click Next
- c. In the Handling Coincidental Samples popup, choose Use Mean and click OK (should not matter, because all coincident points were removed in the initial query).
- d. In the Step 1 of 4 Geostatistical Method Selection dialog box, accept the defaults and click Next
- e. In the Step 2 of 4 Semivariogram/Covariance Modeling dialog box, check the Anisotropy box and click Next
- f. In the Step 3 of 4 Searching Neighborhood dialog box, change Neighbors to Include: to 25, set Shape Type: to the second type from the left (immediately to the right of One Sector) and click Next
- g. In the Step 4 of 4 Cross Validation dialog box, click Finish
- h. Click OK in method summary window.
- 9. Use GA Layer to Grid Tool to create output grid
  - a. Input = GA Layer result from step 8
  - b. Output surface grid = grids\ + segcode + \YY\ MMDDYY\ + 2-letter parameter designation + MMDDYY (for example, grids\vp\07\040904\ch052907)
  - c. Set cell size and Extent to the same as 1a.
- 10. Repeat steps 7, 8, and 9 for salinity(sa mean) and turbidity(tu mean) for the current date.
- 11. Use Multi Output Map Algebra Tool to calculate K<sub>d</sub> grid from salinity, turbidity, and chlorophyll grids.
  - a. Use appropriate equation in expression to calculate  $K_d$ (Perry, 2006).

**Equation 1**. For Segments MPNOH, MPNTF, CHKOH, JMSPH, JMSOH, JMSMH, JMSTF1, JMSTF2, APPTF:

$$K_d = 1.192674757 + 0.295620722 \times \sqrt[1.5]{TU} - .056160407 \times SA + .000274598 \times CH$$

Equation 2. For Segments LYNPH, PMKOH, PMKTF, YRKPH, YRKMH, PIAMH:

$$K_d = 0.5275793536 + 0.3193475331 \times \sqrt[1.5]{TU} + 0.0176700982 \times SA + 0.0271723238 \times CH$$

b. Example expression for yrkph(yp):

kdgrid = 0.5275793536 + 0.3193475331 \* pow(tugrid, 1 / 1.5) + 0.0176700982 \* sagrid + 0.0271723238 \* chgrid

```
where, kdgrid = location and name of output grid(grids\yp\07\052907\kd0052907) tugrid = location of turbidity grid from steps 7-9 (grids\yp\07\052907\tu052907) sagrid= location of salinity grid from steps 7-9 (grids\yp\07\052907\sa052907) chgrid= location of chlorophyll grid from steps 7-9 (grids\yp\07\052907\cho52907\cho52907)
```

12. Determine if each cell in kdgrid meets appropriate K<sub>d</sub> threshold using Multi Output Map Algebra Tool

Table 1. K<sub>d</sub> Thresholds

PLL	Segment	Zones		
		0-	1-	0-
0.22	Polyhaline, Meso haline	1.51	0.76	3.03
0.13	Oligohaline, Tidal Fresh	2.04	1.02	4.08

```
Expression for yrkph(yp) 0-1m:
kdgridt1 = con(kdgrid >1.51, 0, 1)
```

where kdgridt1 = attainment grid for 0-1 meters (grids\yp\07\052907\t1052907) kdgrid = result from step 11 (grids\yp\07\052907\kd052907)

```
Expression for yrkph(yp) 1-2m:
kdgridt2 = con(kdgrid > .76, 0, 1)
```

where kdgridt2 = attainment grid for 1-2 meters (grids\yp\07\052907\t2052907) kdgrid = result from step 11 (grids\yp\07\052907\kd052907)

13. Merge results from step 12 based on depth using Multi Output Map Algebra Tool:

```
Expression for yrkph(yp): kdgrida = con(segbath = = 4, kdgridt2,(con(segbath = = 2 or segbath = = 3, kdgridt1, 0)))
```

```
where, kdgridt1 = result from step 12 for 0-1m (grids\yp\07\052907\t1052907) kdgridt2 = result from step 12 for 1-2m (grids\yp\07\052907\t2052907) segbath = result from step 1b (baselayers\ypbathy)
```

#### $kdgrida = attainment grid (grids\yp\07\052907\a052907)$

- 14. Use the Extract by Mask Tool to remove the exclusion zones from the analysis.
  - a. Input Grid = Result of step 13 (grids\yp\07\052907\a052907)
  - b. Mask Raster = result of step 1c (analysis\ypxz)
  - c. Output Raster =  $(grids \cdot yp \cdot 07 \cdot 052907 \cdot ax \cdot 052907)$
- 15. Combine grids for assessment using Combine Tool
  - a. Input Rasters = cbseg; cusav grd; segbath; kdgridax

Where cbseg = result of 1a cusav grid = result of 1c

segbath = result of 1b

kdgridax = result of step 14

b. Output grid = combine result (grids\yp\ $07\052907\$ wc052907)

- 16. Export results table to Access
  - a. Add the result from step 15 (grids\yp\07\052907\wc052907) to an ArcMap document
  - b. Right click on the grid and select Open Attribute Table
  - c. Click on Option in the lower right hand corner and select export
    - i. Export: all records
    - ii. Save the output table to the access database where water clarity acres will be calculated (gdb = wca.gdb, table = yp052907)
- 17. Calculate water clarity acres
  - a. Open access database where result of step 16 was saved
  - b. Open result from step 16 in design view
  - c. Rename the 4 fields after Count(order of columns dependent on order columns were combined in step 15. If entered in order designated in the this guide:
    - i. 1st Column after Count (YP) should be renamed SEG BNDRY
    - ii. 2<sup>nd</sup> Column after Count (YP CU06) should be renamed CU SAV
    - iii. 3<sup>rd</sup> Column after Count (YPBATH) should be renamed BATHY
    - iv. 4<sup>th</sup> Column after Count\_ (WC052907) should be renamed ATTAINMENT
- 18. Append Tables
  - a. Open wca.gdb
  - b. Create copy of first table (yp052907) and rename it "summary" (This step can also be done in ArcCatalog)
  - c. Close Access
  - d. Open Append Tool
    - Input datasets are all other tables other than the one that was copied in 18a in wca.mdb (yp041907, yp052907, 061307, 070207, 082707, 091307, 101007, 111207)
    - ii. Target dataset is "wca.mdb\summary"

- 19. Calculate water clarity acres
  - a. Open wca.gdb
  - b. Run Query 1
  - c. Run Query 2
  - d. Run Query 3
  - e. Monthly and mean Annual water clarity acres are now located in the table called monthly wca and annual wca, respectively.

Note: These queries are used to calculate water clarity acres by initially converting cell counts of attainment into acreage of attainment inside and outside of current SAV areas for each dataflow cruise. Water clarity acres for the segment are then calculated by the taking the annual mean of the monthly acreage. Total acreage of SAV within the segment's watershed boundary is also calculated.

```
Key for Access Tables (annual_wca & monthly_wca)
WCA = Water Clarity Acres
NSWCA = Water Clarity Acres outside of current SAV
CUSAV + NSWCA = Current SAV + Water Clarity Acres outside of
Current SAV
```

In VA, a segment is in attainment if at least one of three conditions is met.

- 1. Current SAV >= Water Clarity Acreage Goal
- 2. Total Acreage of Attainment >= Water Clarity Acreage Goal
- 3. Current SAV + Acreage of Attainment Outside of Current SAV >= Water Clarity Acreage Goal

Segment goals are defined in DEQ document 9 VAC 25-260 Virginia Water Quality Standards (2005).

These are alternative Steps following 8 and 9 for segments where the use of barriers is appropriate. Follow steps 8 and 9 to create interpolation without barriers. Follow the steps below to interpolate with barriers and then merged to interpolation without barrier to ensure coverage for the all available bottom in the segment:

- 1. Create barrier layer for segment:
  - a. Use Select Tool (Analysis Tools -> Extract -> Select) to create segment polygon (baselayers/potmh\_coa\_seg.shp)
    - i. Input = baselayers/cbsegsplit
    - ii. Output = baselayers/potmh\_coa\_seg.shp
    - iii. Expression = "CBSEG" = "POTMH COA"
  - b. Use Clip Tool (Analysis Tools -> Extract -> Clip) to create segment barrier
    - i. Input = baselayers/potmh\_coa\_seg.shp

- ii. Output = baselayers/potmh coa barrier.shp
- 2. Create shapefile where cruise points with error codes are selected out.
  - a. Add dataflow point feature (wq data.gdb/pc041907p) to blank map document
  - b. Select where ch\_mean > -999. Note how much data may be invalid. Decide if too much data has an associated error code to proceed with interpolation for this dataset. This decision is made with a concern for the amount and spatial distribution of data that will be excluded. In the future, we would like to move toward a less-subjective approach though the use of an associated standard error grid. If the interpolation is not made, that particular date is ultimately thrown out of any annual mean water clarity acreage calculations. If there is sufficient data to continue, clear the selection before continuing with the interpolation.
  - c. With selection still in place, export selected features to shapefile
    - i. Right click on feature in TOC and choose Data > Export data
    - ii. Export: selected features
    - iii. Use same coordinate system as layer's source data
    - iv. Output shapefile: analysis shapefile\pc041907p.shp
- 3. Use aml Kriging function to create interpolation incorporating new barrier file
  - a. Open Single Output Map Algebra tool (Spatial Analyst Tools > Map Algebra > Single Output Map Algebra)
  - b. Expression (make sure to replace '~' with location of file on local machine):

Kriging(~\analysis\_shapefile\pc041907p.shp, ch\_mean, ~\baselayers\potmh\_coa\_barrier.shp, GRID, #, SPHERICAL, SAMPLE, 25, 1500, 25)

- c. Output Grid: ~\grids\pc\041907\tch041907
- d. Set cell size and Extent to the same as analysis grids/pc
- 4. Open Con tool (Spatial Analyst Tools > Conditional > Con) to limit extent of interpolated barrier grid
  - a. Conditional grid: ~analysis grids/pc bath
  - b. Expression: "VALUE" > 1
  - c. Input True Raster: ~\grids\pc\041907\tch041907
  - d. Input False Raster: ~\grids\pc\041907\ch041907
  - e. Output raster: ~\grids\pc\041907\bch041907
- 5. Merge barrier grid with interpolated grid without barriers.
  - a. Open Single Output Map Algebra tool (Spatial Analyst Tools > Map Algebra > Single Output Map Algebra)
  - b. Expression (make sure to replace '~' with location of file on local machine):

Merge(~\grids\pc\041907\bch041907, ~\grids\pc\041907\bch041907)

- c. Output Grid: ~\grids\pc\041907\mch041907
- 6. Repeat this procedure for all parameters

7. To Proceed: delete ~\grids\pc\041907\ch041907 and rename ~\grids\pc\041907\mch041907 to ~\grids\pc\041907\ch041907. Use this renamed merged grid in all future steps (go to step 10 above to continue with water clarity analysis)

#### **Sources**

- Perry, E. (2006). Notes *on Lumping vs Splitting Kd = f(turbidity) calibration*. Unpublished Report.
- 9 VAC 25-260 Virginia Water Quality Standards. (2005). § 62.1-44.15 3a of the Code of Virginia. Retrieved February 21, 2007, from http://www.epa.gov/waterscience/standards/wqslibrary/va/va 3 wqs.pdf.

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Appendix G: CONMON Station QA/QC Protocols in Brief

#### **Continuous Station Coarse QA/QC Protocol**

Step 1 Insert appropriate parameter qualifiers

Parameter	<	>
Temp	-5	45
SpCond	0	100
Salinity	0	70
DO sat	0	500
DO mg/l	0	50
Depth	0	9.10
PH	0	14
Turb	0	1000
Chl	0	400
Fluor	0	100

## Step 2 Identify negative "-" values

All negative values are flagged with a "GNV" in the appropriate parameter a column

### Step 3 Identify time periods when the datalogger or certain probes were not deployed.

In the appropriate parameter a column, flag all nondeployments with a "NND".

### Step 4 Identify and flag single spike NTU values

In the NTU a column, flag all single spike NTU values >300 with "NQR".

## Step 5 Identify and flag single spike Chl values

In the Chl a column, flag all single spike Chl values >400 with "NQR".

## Step 6 Identify and flag single spike %Fluor values

In the Fluor a column, flag all single spike Fluor values >100 with "NQR".

#### **Step 7 Identify and flag probe failures**

In the appropriate parameter a column, flag time intervals with "GPF".

Note: This would apply to DO membrane punctures, pH bulb breakage etc.

# Step 8 Identify and flag time periods in which specific probes failed to meet acceptable post calibration criteria

In the appropriate parameter\_a column, flag time intervals with "GPC".

Note: This would apply to DO drift and similar issues. If you can not clearly identify where the problem began, flag the entire deployment interval.

# Step 10 Identify and flag time periods in which entire instrument or specific probes were out of water.

In the appropriate parameter a column, flag affected time intervals with "NOW".

Note: If entire instrument is out of water, all parameter\_a columns must be flagged.

## Step 12 Identify and flag time periods affected by a time skip.

In the comment column, flag effected time period with "CTS".

#### Step 13 Identify and flag time periods affected by station maintenance.

In the appropriate parameter a column, flag affected time interval with "NQR"

Note: This was seen in some of our turbidity and depth data.

### Step 14 Link deployments and look for probe drifts, significant mismatch, etc

In the appropriate parameter\_a column, flag affected data with the appropriate error code.

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Appendix H: Changes from previous QAPP plan

- 1. Starting in 2008, Winkler titrations using a Hach kit were no longer performed for dissolved oxygen verification samples during both DATAFLOW cruises and CONMON sonde switchouts.
- 2. In 2007 and 2008 all instruments deployed at Rappahannock and Potomac CONMON stations were YSI 6600EDS V2 sondes, using the ROX optical dissolved oxygen probes. From March 5 through April 10, 2009, a 6600EDS V2 sonde was deployed as normal in the Rappahannock tidal fresh segment (RPPTF) at Hicks Landing. However, due to limited funding and the initiation of the Rappahannock vertical profiler, the 6600EDS V2, which had been deployed at Hicks Landing, was moved to the Rappahannock vertical profiler. A 6600EDS using the rapid pulse (Clark cell type) dissolved oxygen probe was put back in at Hicks Landing on April 10, 2009.